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PHOTOGRAPHIC SCIENCE AND ENGINEERING
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Layer Thickness of Photographic Emulsions and Image Definition

H. F. NITKA AND A. J. DERR, *Research Laboratories, Ansco, Binghamton, N.Y.*

Acutance and line frequency response are determined for a typical fine-grain positive and a coarse-grain negative emulsion, both coated at various thicknesses and different coating weights. Light scattering and shape of characteristic curve influence predominantly acutance, while granularity and light scattering are important factors in limiting frequency response.

The reproduction of fine details in a photographic emulsion cannot be predicted from its sensitometric characteristics alone which generally describe only its ability to reproduce relatively large image areas of at least several hundred microns extension. Small details are usually reproduced with a reduced contrast which, for very fine details, can suppress detail recognition in the reproduction below the contrast threshold of the observer. Further, the grainy structure of a developed silver image of low contrast can reach such an extent that it covers up completely the fine detail. The main reason for image degradation, in addition to the grainy image structure, is the scattering of the exposing light within the photographic emulsion. This light scattering depends on several factors: wavelength; number, shape, and size distribution of the silver halide crystals; absorption of the incident light within the layer, and its refractive index. Several workers attempted the qualitative and quantitative determination of the importance of light scattering and its influence on image definition. In the past, resolving power was frequently used as a criterion for image definition. But recent literature on this topic shows clearly that resolving power alone is not capable of describing completely this complex aspect of image definition,[1] and acutance and frequency response were shown to analyze the problem much more satisfactorily.[2]

In the following some results will be reported on the influence of both silver halide content and layer thickness on acutance and frequency response of a slow

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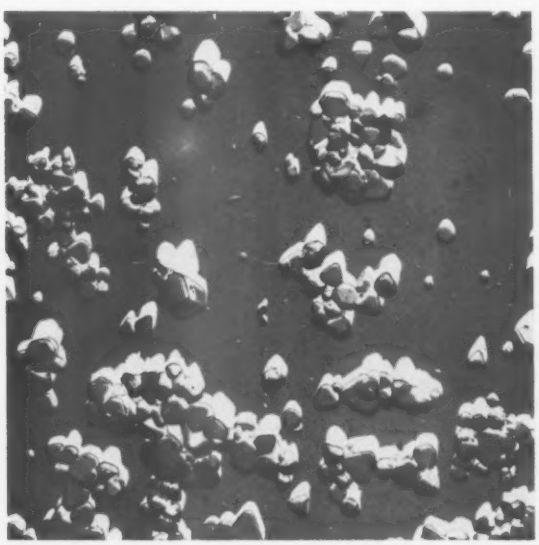

Fig. 1a. Grain structure of cine positive emulsion, × 5,000.

Fig. 1b. Grain structure of fast negative emulsion, × 5,000.

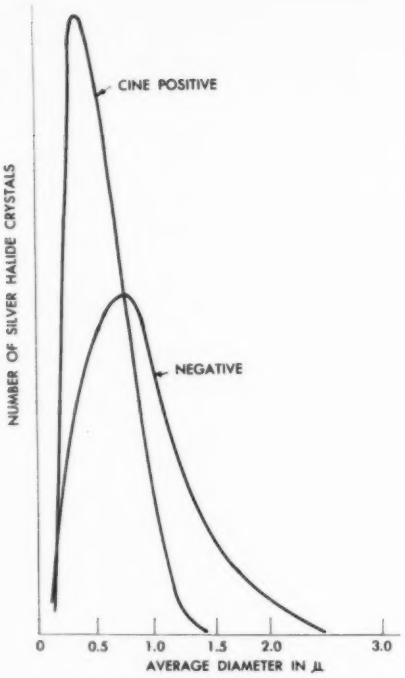

Fig. 2. Silver halide crystal size distribution.

cine positive and a fast negative emulsion. These results will then be discussed on the basis of current literature and theory.

Experimental Conditions

Emulsion Properties

Two silver bromide-iodide emulsions were used in this investigation — a slow fine-grain cine positive emulsion (2 mol % iodide) and a fast coarse-grain negative emulsion (5 mol % iodide). Figures 1a and 1b show electronmicrographs of the silver halide crystals, and Fig. 2 their crystal size distributions. The distribution curves peak at approximately 0.4 μ and 0.8 μ crystal diameter respectively. The positive emulsion contains barely any crystals larger than 1.2 μ diameter, and the largest crystals of the negative emulsion extend to a diameter of up to 2.5 μ. These emulsions are optically unsensitized and coated at various thicknesses on a triacetate filmbase backed with an effective antihalation protection against blue light. Two series of emulsion coatings are used: One series varies the thickness of the layer while maintaining constant the silver halide concentration per unit volume, i.e. doubling the layer thickness means twice the amount of silver halide per unit area. Another coating series varies the layer thickness merely by dilution with gelatin, thus retaining a constant amount of silver halide per unit area. Table I provides some detailed information on the emulsion layers.

TABLE I

Average Layer Thickness in μ	Constant Ag/Unit Area, mg Ag/100 sq cm		Constant Ag/Unit Volume, mg Ag/100 sq cm
	Cine Positive	Negative	Cine Positive & Negative
4.6	—	—	13.5
9.5	33	29	28.0
14.5	37	34	41.6
18.3	37	34	55.0
25	—	—	72.0

Sensitometric Conditions

The characteristic curves of all layers are determined in an intensity-scale sensitometer, and are shown in Figs. 3a–d. Cine positive is developed for 5 min in Ansco A20 Developer; the negative for 5 min in Ansco Permadol Developer. The contrast is seen to increase with increasing layer thickness in the coating with constant silver content per unit volume. Increasing the layer thickness while maintaining the silver content per unit area does not change the characteristic curve.

Acutance Measurements

Using a recording microdensitometer, acutance is determined from knife-edge exposures according to the procedure described by Higgins and Jones[3] and Higgins and Wolfe.[4] The mean square gradient $(G^2)_{av}$ of a microdensitometer trace divided by the density difference ΔD of the knife-edge is used as a measure of acutance. The measurement is carried out at a constant log exposure level measured from the toe of the characteristic curve.[5] These measurements are identical with those taken at a constant density level only in the case of the coating series with constant silver per unit area due to the similarity of the characteristic curves for various layer thicknesses.

Each acutance value is based on the average of five microdensitometric tracings of knife-edge exposures.

Frequency Response

Instead of determining the resolving power with the conventional bar pattern, the films are evaluated for their frequency response. The theory of this measurement is described by Schade,[6] Eyer,[7] and Higgins and Perrin.[8] Accordingly, the sine-wave response can be derived from a knife-edge exposure, as described by Eyer.[7] The film is treated as a linear system. This approximation is sufficiently valid for purposes of comparison and also compensates for the gradient differences in the constant silver halide per unit volume series.

The result of such an evaluation is a spatial frequency-response curve shown in Fig. 4. The abscissa indicates the frequency in lines/mm, and the ordinate the relative response to sine-wave exposure modulation. Both variables are generally plotted on a logarithmic scale. The response at low frequencies is identical with macroscopic film response. For increasing frequencies the deviations from the macro-

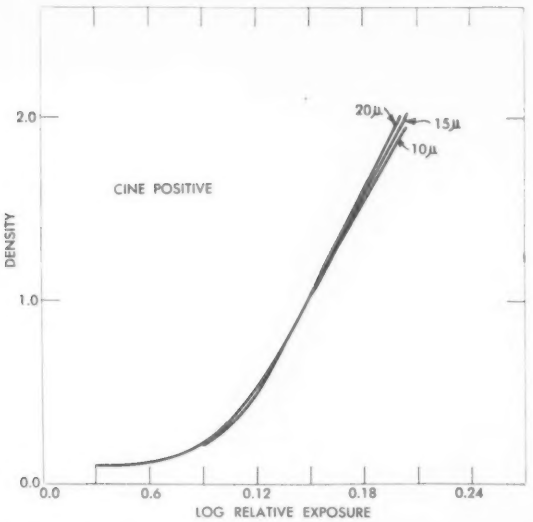

Fig. 3a. Sensitometric H & D curves, constant coating weight and variable thickness, cine positive.

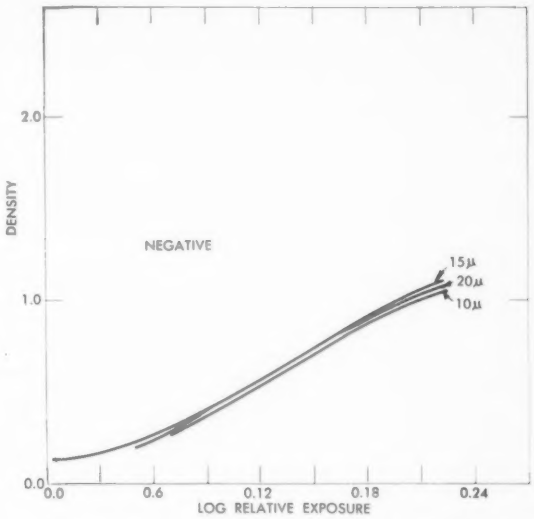

Fig. 3b. Sensitometric H & D curves, constant coating weight and variable thickness, negative.

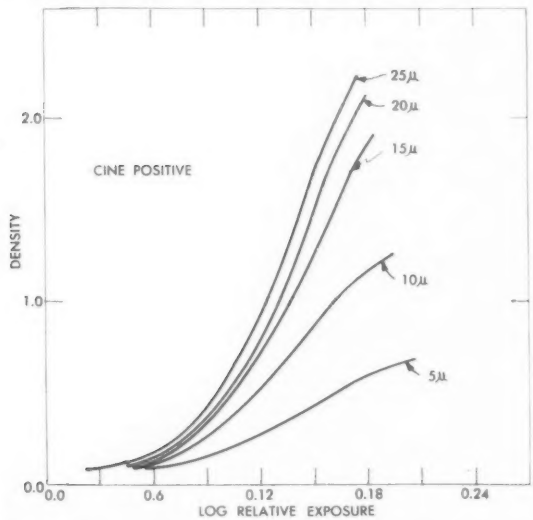

Fig. 3c. Sensitometric H & D curves, constant silver halide content per unit volume and variable thickness, cine positive.

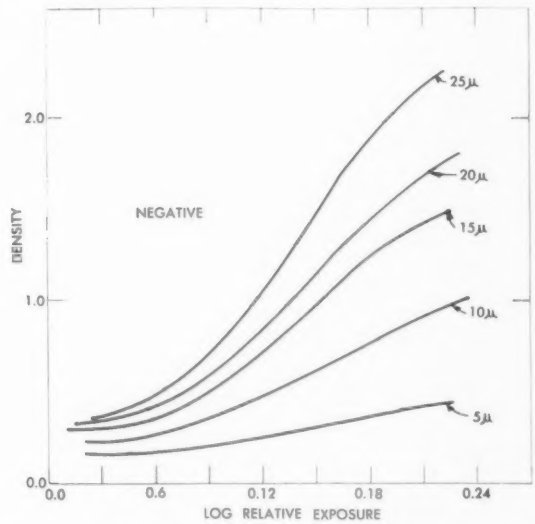

Fig. 3d. Sensitometric H & D curves, constant silver halide content per unit volume and variable thickness, negative.

scopic characteristics become more and more significant.

Although the curves show some response up to very high frequencies (high resolving power), the practical limit is determined by the visual response and taken at 0.04 or 4%. This value corresponds closely to the threshold limit of the eye with respect to the discrimination of small detail brightness differences. This limit is valid only in a practically grain-free system. The graininess of the photographic emulsion behaves like "noise" in a communication system. The true limit of the frequency response, i.e., the visual resolving power, then depends on the graininess of the system. From granularity data (mean square deviation of density fluctuations) the limit of response of the cine positive is estimated at approximately 5% and for the high-speed negative at 10%. The latter is a typical coarse-grain emulsion.

Optical Density of Unprocessed Emulsion Layers

The measurement of the diffuse density of the unexposed and unprocessed emulsion layers provides some information on the relative amount of the light scat-

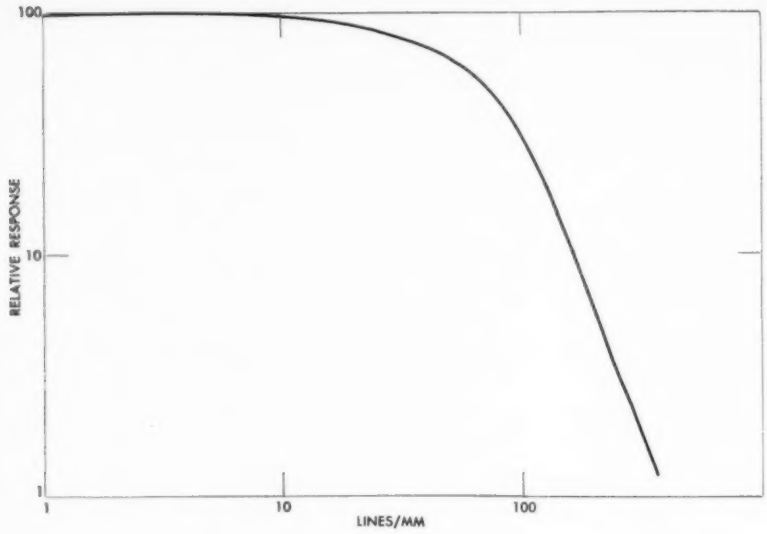

Fig. 4. Schematic frequency-response curve

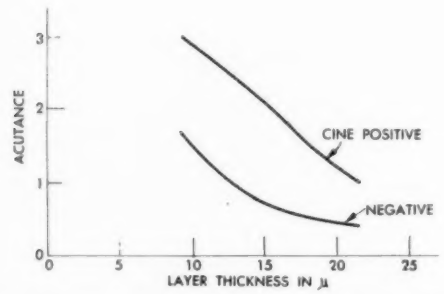

Fig. 5. Acutance vs. thickness for constant silver halide content per unit area.

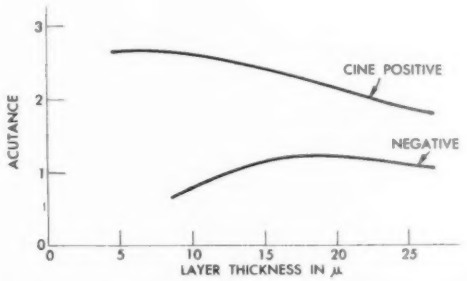

Fig. 6. Acutance vs. thickness for constant silver halide content per unit volume.

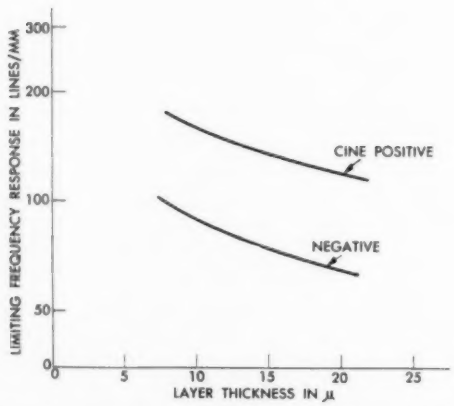

Fig. 7. Limiting frequency response for constant silver halide content per unit area.

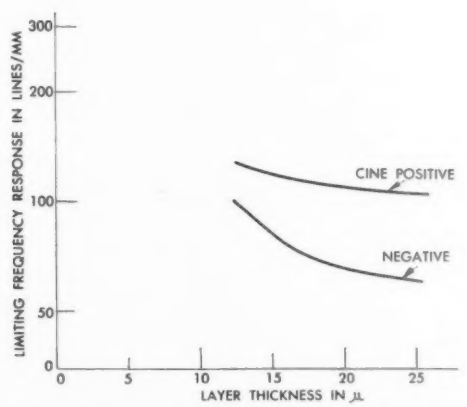

Fig. 8. Limiting frequency response for constant silver halide content per unit volume.

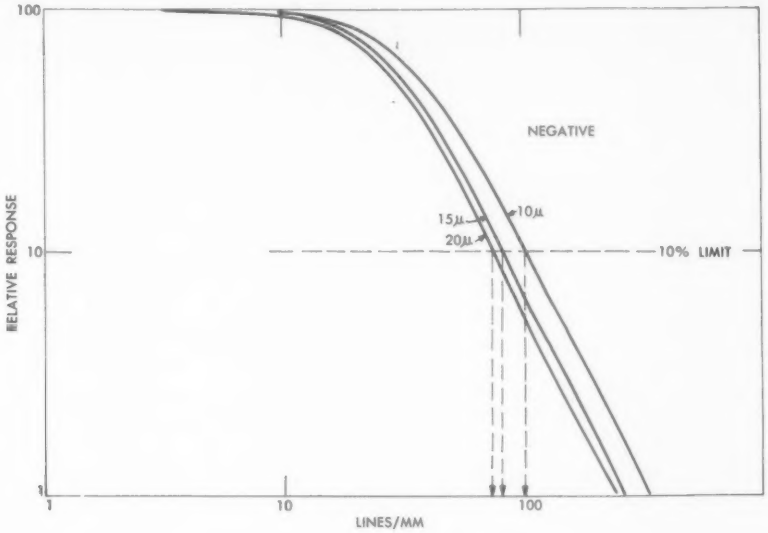

Fig. 9. Example of frequency response for various layer thicknesses.

tered within the emulsion. Since the emulsions used are optically unsensitized, the spectral distribution of the blue light used for these measurements resembles closely the intrinsic light sensitivity of the silver halide crystals.

Results

Acutance

The results are shown in Figs. 5 and 6. For a constant amount of silver halide per unit area the acutance decreases rapidly with increasing coating thickness (Fig. 5). Since the contrast for a particular emulsion is independent of the layer thickness in this series of experiments, this result indicates that the exposing light diffuses more the longer it has to travel through the layer. As expected the acutance of the positive emulsion is considerably higher than that of the negative emulsion due to its higher intrinsic contrast and different shape of its characteristic curve.

For a constant silver halide content per unit volume, however, the acutance shows relatively little variations with coating thickness (Fig. 6). It appears that the beneficial effect of improved contrast for heavier silver halide deposits is counteracted by an increased diffusion of light within the layer.

It must be expected that the exact behavior of any emulsion will depend on the many factors influencing light scattering, and on the contrast and shape of the characteristic curve. But the results found for the two coating series are somewhat characteristic in demonstrating the relative influence of the important factors determining acutance.

Frequency Response

Similar results are obtained for the frequency response of the two coating series, though they seem to be less pronounced than those for acutance.

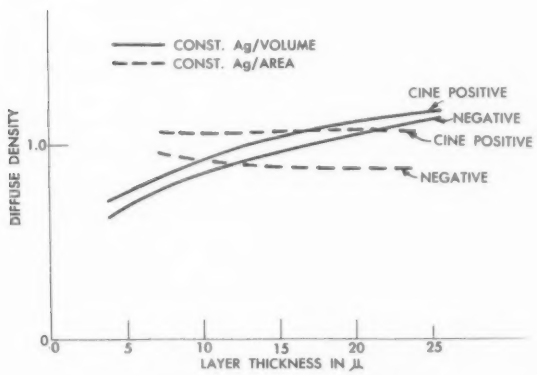

Fig.10. Diffuse density of unprocessed layers.

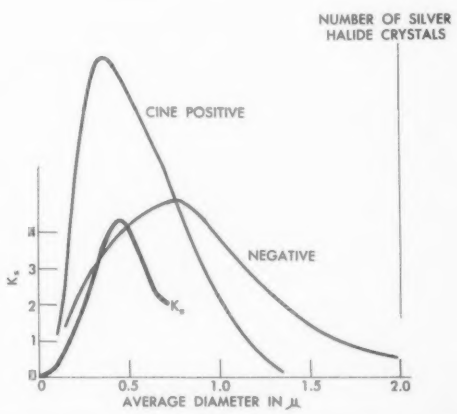

Fig. 11. Light scattering coefficient K_s for silver bromide crystals in gelatin.

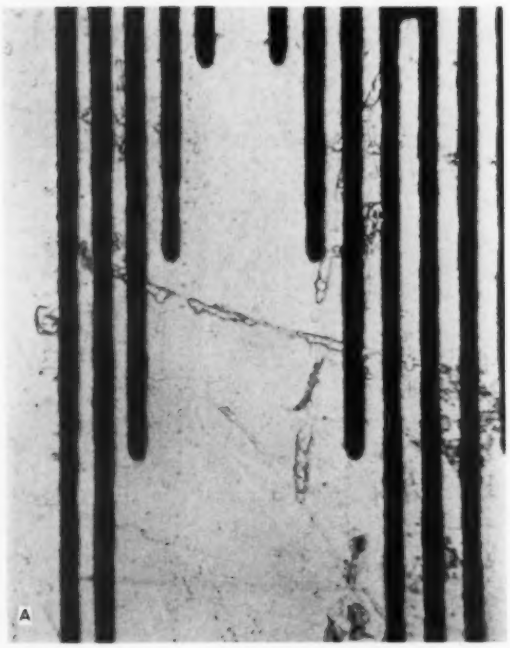

Fig. 12a. Bar pattern original for prints on test emulsions, × 140.

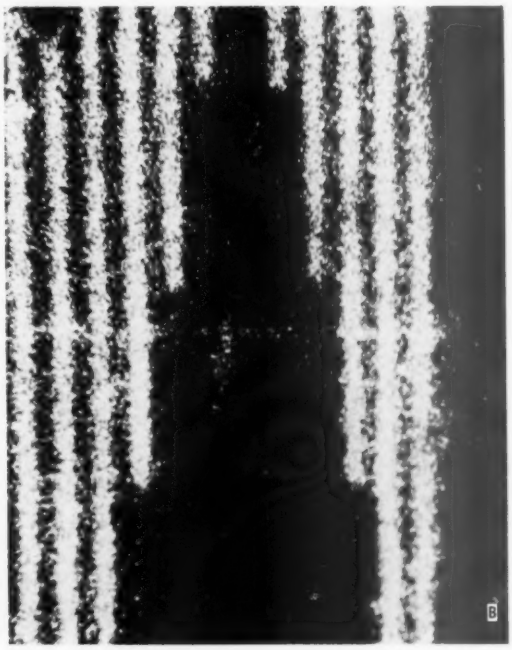

Fig. 12b. Print of bar pattern on cine positive test emulsions, × 140

Figure 7 shows the limiting frequency response for constant silver content per unit area. The limiting frequency decreases for increasing layer thickness, possibly due to increasing light diffusion for thicker layers.

The change of frequency response with layer thickness and silver concentration (constant amount of silver halide per unit volume) is illustrated in Fig. 8 and shown to be less pronounced than in the case of constant silver halide content per unit area.

Figure 9 gives an example of the frequency response for the negative emulsion with varying silver halide content per unit volume.

Optical Density of Unprocessed Emulsion Layers

The diffuse density of an unexposed and unprocessed emulsion layer can be used as a criterion for the amount of scattered light.

From Fig. 10 it is seen that for constant silver halide content per unit area the diffuse density hardly changes with layer thickness. This means that the total amount of scattered light is the same for different layer thicknesses. This is to be expected because the number of light scattering centers is the same, irrespective of thickness. The fact, however, that the acutance is reduced for thick layers indicates clearly that the same amount of scattered light spreads out wider within thick layers.

For layers with a constant amount of silver halide per unit volume, the diffuse density rises fast with increasing thicknesses, due to the increasing number of light-scattering silver halide particles. In other words, the amount of scattered light increases with thickness as is suspected from the results on acutance: heavier scattering for high coating weights offsets the advantages of increased contrast.

The observation that the relative amount of scattered light is higher for the positive emulsion than that for the negative emulsion (for equal coating weight) will be discussed in the next section.

Discussion

Frieser[9] has published recently a series of papers on the reproduction of small details by various photographic layers. He determines the extinction coefficient for light within a photographic emulsion from the effective light intensity distribution around small areas (slit, circular aperture) of various dimensions. Frieser concludes that the amount of scattered light relative to non-scattered light increases with thickness, both for layers with constant coating weight and with increasing silver halide content. This result agrees well with the conclusions reached in the preceding section, where the decrease of acutance with increasing layer thickness is related to light scattering.

Frieser[9] and Klein[10] also demonstrate that the extinction coefficient of photographic emulsion layers reaches a maximum for an average silver halide crystal size of about 0.2 to 0.3 μ diameter, and Frieser[9] shows that the diffuse density of an emulsion layer with constant coating weight is highest for an average crystal size of 0.4 μ. However, since the crystal size is never uniform in a photographic emulsion, the presence of small crystals in a coarse-grain emulsion tends to render the maximum of light scattering less

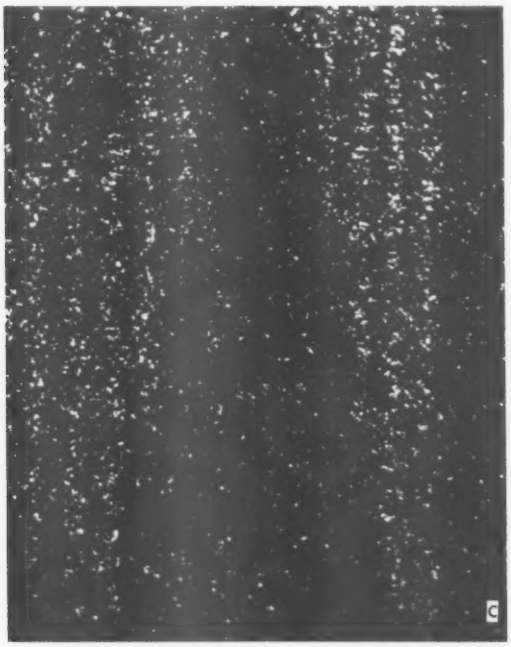

Fig. 12c. Print of bar pattern on negative material, × 140.

pronounced. Really fine-grain emulsions (e.g. Lippmann emulsions) show very little light scattering and are almost transparent. In Fig. 11 the scattering coefficient K_s for blue light is plotted together with the size distribution of the two emulsions used in this investigation. K_s can be calculated from the "NBS Light Scattering Tables"[11] for a relative refractive index of $m = 1.47$ (m = Refractive Index for AgBr/Refractive Index for Gelatin). The blue light scattering reaches a maximum for particles having a diameter of 0.43 μ.

It is seen that the maximum of the crystal size distribution of the cine positive emulsion is closer to the scattering maximum than that of the negative emulsion; therefore, for equal coating weight, the positive emulsion is expected to scatter light somewhat more than the negative emulsion. This agrees with the observations on diffuse density described in the section immediately above.

A few remarks may summarize the significant factors determining acutance and limiting frequency response, i.e. visual resolving power: Light scattering within the layer and the shape of the characteristic curve of the emulsion appear, from the foregoing results, to play a predominant role in acutance. The limiting frequency response, however, by virtue of its calculation from a linearized characteristic curve, depends mainly on the granular structure of the image, apart from light scattering. It follows from Fig. 9 that any increase in granularity raises the threshold for recognizing a signal and, thus, decreases resolving power. If a 5% threshold were assigned to the coarse-grain negative emulsion, it would have the same and, in the case of very thin layers, even a higher visual resolving power than the positive emulsion. This would be contradictory to experience, and it illustrates the importance of graininess in resolving power determinations (see Fig. 12). On the other hand, granularity does not greatly influence acutance. Tests on an experimental high-contrast, coarse-grain negative emulsion resulted in acutance values which were superior to that of the positive emulsion, mainly because of the shape of its characteristic curve and a higher intrinsic absorption of scattered light within the layer. It is well known that increased absorption[12] (e.g. by adding a dye) reduces light scattering and improves acutance, irrespective of a grainy image structure.

Acknowledgments

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Effect of Gelatin Layers on the Dimensional Stability of Photographic Film

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Photographic films made with the more dimensionally stable supports, such as polystyrene, undergo small but significant size changes caused by the gelatin emulsion and gelatin backing layers. Some of the physical properties of these gelatin layers, measured on specimens stripped from a special base, are described. It is shown how the thickness, elastic modulus, humidity expansion, hysteresis, moisture relaxation, and stress relaxation of the gelatin layers affect the dimensional stability of the supported film. The modulus of the emulsion decreases on photographic processing and is very dependent on relative humidity. An unusual type of "reversed" dimensional hysteresis is described which is peculiar to gelatin-coated films on moisture-resistant supports. This effect is shown to have a major influence on the dimensional change of the film during processing.

New types of photographic film support made from various synthetic high polymers, such as polyvinyl chloride, polystyrene and polyesters, have come into general use in recent years. This has been so primarily in the graphic arts field, because of superior moisture resistance and improved dimensional stability. These materials permit closer registration in color work and more accurate reproduction of scale drawings without the difficulties involved in using glass plates. No photographic film is absolutely stable in dimensions, and the synthetic high polymer films will expand or shrink a few hundredths of a percent under some conditions. This can be troublesome if uncontrolled, particularly with large films. For example, a size change of only 0.02% is equal to 0.008 in. in a 40-in. sheet, which is more than can be tolerated in some applications. As these new films attain wider use where dimensional stability is critical, it becomes increasingly important to understand the nature of these small size changes and the manner in which they can be minimized.

It has been pointed out previously that gelatin emulsions increase the humidity coefficient of linear expansion and also the permanent shrinkage of photographic film.[1] This is because the gelatin exerts a lateral compressive force on the base when dry and literally squeezes it into a smaller size. The effect of the emulsion and base thickness on dimensional stability was illustrated by Centa,[2] and a theoretical relationship was derived by Umberger.[3] Hysteresis has also been mentioned as a phenomenon responsible for small dimensional changes in film.[1] With cellulose ester film supports the dimensional effects caused by gelatin layers are of secondary importance to the base shrinkage, but with the more moisture-resistant high polymer supports used in critical applications, such factors must be considered.

It is the purpose of this paper to describe some of the physical properties of gelatin emulsions and gelatin non-curl backing layers which affect the dimensional stability of low-shrink photographic films. Although polystyrene support was used in this investigation, the conclusions reached concerning the effect of gelatin apply as well to films on other low-shrink supports. Part I deals with the properties of the unsupported gelatin layers alone, and Part II deals with their effects on the dimensional behavior of the complete film.

Experimental Procedure

Two different types of graphic arts films on polystyrene base were used for this investigation:

	Nominal base thickness, mils	Nominal emulsion thickness, mils
Kodalith Ortho PB Film		
Type 2	5	0.30
Type 3	5	0.25
Kodak Commercial PB Film	10	0.70

Both Kodalith and Commercial films have a dyed gelatin backing layer (for antihalation and curl control) which has approximately the same thickness as the respective emulsions. Kodalith emulsion is quite thin, hard, and has a high silver/gelatin ratio; whereas Commercial emulsion is relatively thick, soft, and has a low silver/gelatin ratio. These differences are due to photographic requirements, but they also

Presented at the Annual Conference, Rochester, N.Y., 9 October 1958. Received 12 September 1958.

affect the physical characteristics of the emulsions and the dimensional stability of the films.

During the course of this work, Type 2 Kodalith emulsion was replaced by Type 3 to provide photographic improvements; therefore, some data were obtained on each. However, both types have essentially the same physical properties except that Type 3 is slightly thinner.

Regular production lots of film were used wherever possible. In order to determine the effect of gelatin thickness on some film properties, it was necessary to make special coatings. In most work on unsupported gelatin layers reported in the literature, specimens for study were obtained by making hand coatings about 5 mils thick on glass plates. It has been our experience that this technique yields gelatin films having significantly different properties from those of normal photographic film coatings which are only $^1/_5$ to $^1/_{20}$ of this thickness. This difficulty was overcome in the present work by coating the emulsion or backing on a special film base having a very weak adhesive layer from which the gelatin coating could be readily stripped after drying. In the case of Kodalith emulsion and backing, the thickness was increased to 0.6 mils to facilitate handling of the stripped layer.

All special coatings were made using standard gelatin emulsion or backing and were applied on a pilot plant coating machine which was operated as closely as possible to commercial conditions. The coatings were then stored at 70°F and 50% RH until used.

The dimensional change measurements were made on 35mm × 12-in. specimens by means of a pin gage.[1] In the case of unsupported gelatin layers, it was necessary, because of their extreme thinness, to reinforce the ends of the specimens with adhesive tape before perforating the holes to fit the gage pins. For measuring these materials the gage tension was reduced from the normal 150 grams to 50 grams by counter-balancing. For unsupported gelatin layers, five specimens were measured and the results averaged; for supported films the results for three specimens were averaged. The accuracy of the dimensional change measurements is considered to be ± 0.03% of the dimension for unsupported gelatin layers and ±0.005% for supported films.

Since thickness measurements on the very thin gelatin layers are critical, special precautions were taken. Unsupported gelatin layers were measured with a dial micrometer to 0.00002 in. and the average of five measurements on individual samples recorded. Supported gelatin layers were measured by means of a microscope on sections of film cut with a microtome.

All conditioning of specimens was done in constant humidity rooms controlled to ±1.0% RH and ± 0.5° F. Sufficient time was allowed for equilibrium, usually two hours. Occasionally the conditioning time had to be extended overnight because of practical considerations.

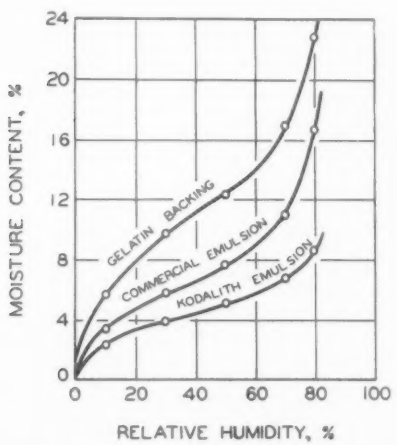

Fig. 1. Equilibrium moisture sorption of various unsupported gelatin film layers at 70°F.

Part I—Physical Properties of Unsupported Gelatin Layers

As mentioned before, the effect of gelatin layers on the dimensional stability of photographic film depends on the compressive forces they exert on the base. This is determined primarily by the thickness, humidity expansion, and modulus of elasticity of each layer. Several other factors are also involved, and an understanding of the subject is aided by first discussing moisture sorption relationships and the phenomena of moisture relaxation and hysteresis.

Moisture Sorption

The moisture sorption of gelatin at various relative humidities is a determining factor in its mechanical and dimensional properties. Moisture sorption curves for the various film layers used in the present study are shown in Fig. 1. The difference in equilibrium moisture content between the two gelatin emulsions and the gelatin backing layer is due to the difference in composition, principally the amount of silver halide. The very high moisture sorption of all the gelatin layers compared with polystyrene base, which has a maximum moisture take-up of less than 0.1%, is one of the reasons for the adverse effect which gelatin has on the dimensional stability of photographic film. However, it will be shown later that the dimensional and mechanical properties of gelatin layers are affected by other factors as well as the moisture content.

Moisture Relaxation

Gelatin layers exhibit a phenomenon which may be described as moisture relaxation. This is a contributing factor in the small dimensional changes which occur in low-shrink photographic films.

Some years ago, C. D. Tate[4] observed that the curl of a single-coated photographic film permanently increased when conditioned for an hour or two at high relative humidity (above 60% RH). This could be explained most readily by a shrinkage of the glelatin emulsion. It was soon established that the gelatin did indeed shrink under these conditions, and since

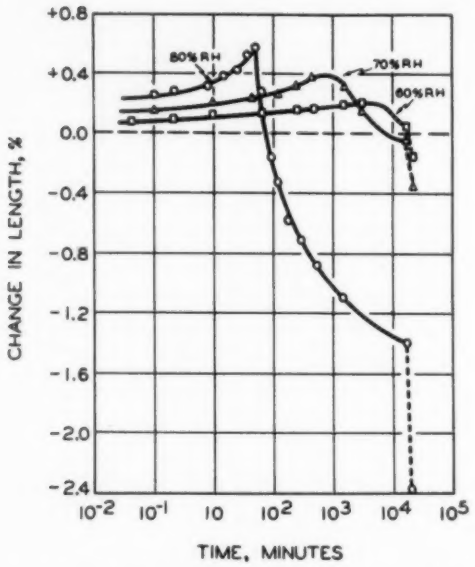

Fig. 2. Relaxation of unsupported Kodalith emulsion as a function of time after raising the relative humidity from an initial condition of 50% RH. Temperature, 70°F. (Broken lines indicate return to 50% RH.)

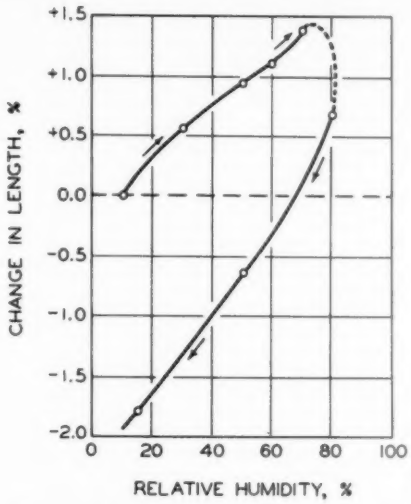

Fig. 3. Dimensional change of unsupported Kodalith emulsion through the first sorption and desorption cycle at 70°F. Conditioning time at each humidity, 2 hours.

no change in weight occurred, shrinkage was not due to the loss of any volatile material.

Figure 2 shows the change in length of unsupported Kodalith emulsion specimens, as a function of logarithmic time after raising the relative humidity from an initial condition of 50% RH. The gelatin first lengthens as moisture is sorbed at the higher relative humidity; it then shrinks, first rapidly, and then at a decreasing rate over a period of several hours. The higher the relative humidity, the sooner the maximum length increase occurs, and the greater is the subsequent rate of shrinkage. When the samples are returned to the starting relative humidity (50% RH), a net shrinkage is observed. This shrinkage amounts to about 0.2% for the sample conditioned at 60% RH, 0.4% for the sample conditioned at 70% RH, and 2.4% for the sample conditioned at 80% RH.

Figure 3 illustrates the dimensional changes which occur on the first humidity cycle when an unsupported emulsion is conditioned at a succession of relative humidities starting at 10% RH. A closed hysteresis loop is not obtained because of the relaxation shrinkage which unavoidably occurs at the high conditioning relative humidities. The relaxed gelatin also exhibits a larger humidity coefficient than the unrelaxed gelatin.

The relaxation shrinkage exhibited by dried gelatin layers at high relative humidities is analogous to that observed by Leaderman[5] when a cellulose filament is stretched while wet and dried under tension. When rewet, the filament shrinks. Leaderman describes this phenomenon as "swelling recovery" and points out the similarity to "thermo-recovery" or relaxation shrinkage at increased temperature. This occurs when high polymers, such as rubber or thermoplastic resins, are stretched while hot, cooled under tension, and then reheated after removal of the external stress. In both cases, the polymer molecules are stretched and then "frozen" in position either by drying or cooling. When "unfrozen" at a later time by moisture or heat, the molecules are free to contract to their preferred position.

When gelatin layers coated on film base are dried, most of the lateral shrinkage is restricted by the base, and this may be considerd equivalent to stretching

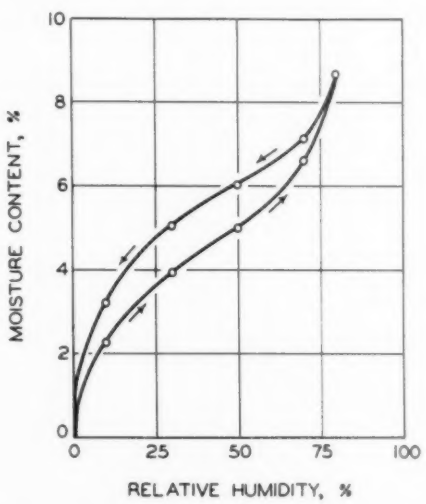

Fig. 4. Moisture hysteresis loop for unsupported Kodalith emulsion at 70°F.

the gelatin. In other words, a structure is established during the drying of the gelatin in which the molecules remain extended.[6,7] When stripped from the temporary base and rehumidified, the internal viscosity of the gelatin is lowered sufficiently for the extended molecules to contract, and the specimen shrinks.

Hysteresis

Gelatin, like paper and other moisture absorbing materials, exhibits hysteresis when subjected to a sorption-desorption humidity cycle.[8] That is, the amount of moisture which the gelatin contains at equilibrium is greater when a given relative humidity is approached from above than when it is approached from below. A moisture hysteresis loop for unsupported Kodalith emulsion is shown in Fig. 4. Moisture hysteresis has the appearance of a lag in the attainment of equilibrium, but conditioning times appreciably longer than the two hours used in the present experiment do not eliminate it. Various theories to account for moisture hysteresis in high polymers are discussed in the literature.[9]

A similar hysteresis curve is obtained if the change in length of an unsupported gelatin emulsion, after having been relaxed at a high humidity, is followed through a humidity cycle, as shown in Fig. 5. The emulsion layer is longer on the desorption part of the cycle than on the sorption side. This parallels the change in moisture content (Fig. 4). The dimensional hysteresis curve for the gelatin backing used on Kodalith Ortho PB Film (not shown) is virtually identical with that of the emulsion. This behavior will be referred to again in a later section.

Humidity Coefficients

The humidity coefficients of linear expansion of unsupported emulsions and gelatin backings may be determined from the change in length between two specified relative humidities. It is customary to determine humidity coefficients from the sorption part of the cycle, and this was done to obtain the data given in Table I. The humidity coefficients of the three gelatin materials studied are similar. Processing and redrying results in a higher humidity coefficient. Relaxation of the unprocessed gelatin at high relative humidity produces the same effect.

The humidity coefficient of expansion of an unsupported gelatin emulsion or backing is several hundred times that for polystyrene base. This is an important factor in the dimensional stability of photographic film.

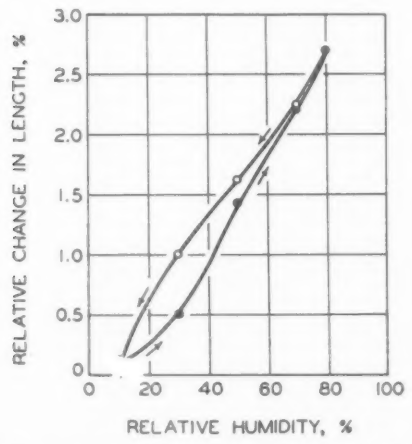

Fig. 5. Dimensional hysteresis loop for unsupported Kodalith emulsion at 70°F after relaxation at 80% RH.

TABLE I
Humidity Coefficients of Expansion of Unsupported Gelatin Layers at 70°F

Material	Thickness, mils	Humidity coefficients of expansion, 10^{-5} in./in./1% RH: Before relaxation	After relaxation at 80% RH
Kodalith Ortho Type 3 Emulsion			
Unprocessed	0.68	24	30
Processed black	0.54	40	40
Processed clear	0.43	48	48
Kodak Commercial Emulsion			
Unprocessed	0.60	34	50
Processed black	0.54	42	46
Processed clear	0.52	46	46
Gelatin backing			
Unprocessed	0.63	30	41
Processed clear	0.54	43	45
Polystyrene support	5.0	0.1	—

The gelatin layers were stripped from the base at 50% RH, and the humidity coefficient determined from the linear expansion between 10% and 70% RH, except for unprocessed Commercial emulsion which was determined between 10% and 60% RH because of relaxation shrinkage above 60% RH.

Modulus of Elasticity

The Young's moduli of the unsupported emulsion and backing layers were determined with an Instron tensile machine at several relative humidities at 70°F. The moduli at 10% RH are given in Table II for three gelatin layers and for polystyrene support. At this low relative humidity the gelatin layers have a much higher modulus than the base, and the emulsions have a higher modulus than the gelatin backing. When processed to give zero silver density (clear), the emulsion modulus decreases to the same level as that of the gelatin backing. When processed to maximum density (black), the Young's modulus is reduced, but not as much as when processed clear. The original silver halide in the emulsion, and to a lesser extent the reduced silver left after processing black, imparts increased stiffness to the gelatin. This phenomenon is analagous to the increase in modulus of plastics upon the addition of inert fillers.[10]

The effect of relative humidity on the moduli of the

TABLE II

Effect of Photographic Processing on the Young's Modulus of Unsupported Gelatin Layers Compared with Film Support at 70°F–10% RH

Material	Young's Modulus, 10^5 psi		
	Unprocessed	Processed black	Processed clear
Kodalith Ortho Type 3 Emulsion	11.0	10.3	8.0
Kodak Commercial Emulsion	10.5	9.3	8.2
Gelatin backing	8.1	—	7.9
Polystyrene support	4.9	—	4.9

Tests made on Instron tensile machine according to A.S.T.M. Method D882-56T, Method A. Rate of straining, 0.1 in./in./min.

two emulsions and the gelatin backing (unprocessed), compared with polystyrene support, is shown in Fig. 6. The modulus of the polystyrene base is independent of humidity; whereas the moduli of the gelatin layers decrease very rapidly above 60% RH. This effect of humidity on the modulus of the emulsion is directly related to its moisture sorption (Fig. 1) and plays an important part in the dimensional stability of the film.

Part II — Effect of Gelatin Layers on the Dimensional Behavior of Film

The influence of the gelatin layers on the dimensional characteristics of film is described in the following sections, from the standpoint of relative humidity, processing, and aging effects. Thermal expansion has not been included because it is primarily a support property. Dimensional hysteresis due to moisture is discussed first because this is essential to an understanding of humidity coefficients and processing dimensional changes.

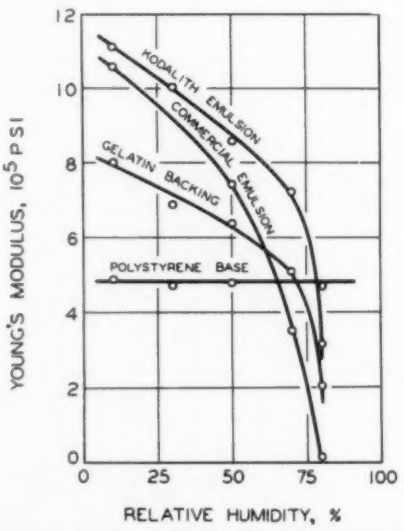

Fig. 6. Effect of relative humidity on the Young's modulus of unprocessed gelatin layers compared with polystyrene base. Rate of strain, 0.1 in./in./min at 70°F.

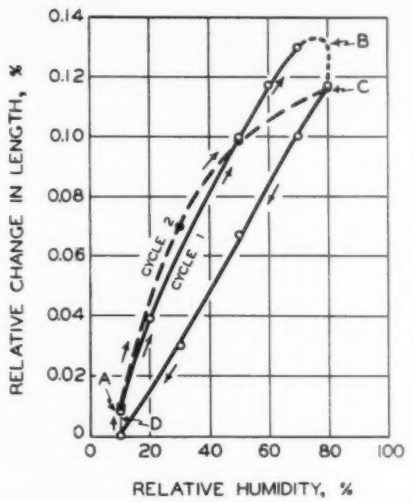

Fig. 7. Dimensional hysteresis loop for unprocessed Kodalith Ortho PB Film, Type 2, at 70°F.

A — Start of first sorption cycle.
B — Shrinkage due to moisture relaxation of gelatin.
C — Point of mechanical equilibrium between gelatin and base.
D — Expansion due to stress relaxation of gelatin.

*Dimensional Hysteresis**

A dimensional hysteresis curve for Kodalith Ortho PB Film is shown in Fig. 7 and illustrates several curious phenomena. The sorption curve in the first humidity cycle exhibits a break between 70% and 80% RH. This is caused by the moisture-induced relaxation shrinkage of the two gelatin layers and the sharp decrease in elastic modulus as described earlier. The magnitude of the relaxation shrinkage of the supported film at 80% RH, of course, is much less than that of the unsupported emulsion (Fig. 3). On the second humidity cycle a closed hysteresis loop is obtained. In the case of Commercial PB Film (data not shown), the break in the first sorption curve occurs between 60% and 70% RH. This demonstrates how errors can occur if humidity coefficients are calculated arbitrarily over certain ranges in relative humidity.

The second peculiarity of the dimensional hysteresis curves shown in Fig. 7 is that the sorption curve falls above the desorption curve. This is opposite to the normal moisture hysteresis (Fig. 4) and also opposite

* Since the phenomenon described here is opposite in direction to normal moisture hysteresis, there may be some confusion in calling it *hysteresis*. However, no better term is known, and for the purpose of this paper, *dimensional hysteresis* will be used to mean a failure of the film to return to the same dimensions when a given relative humidity is approached from opposite directions.

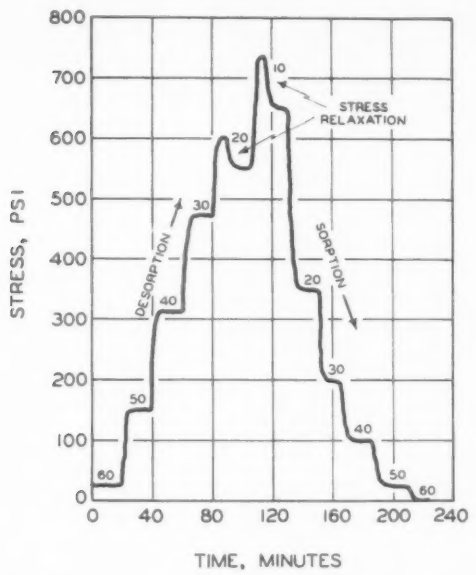

Fig. 8. Change in tensile stress with time at constant strain during the desorption and sorption of moisture in an unsupported, processed Kodalith emulsion at 70°F. Numbers are percent relative humidity. Measurements made on Instron tensile machine.

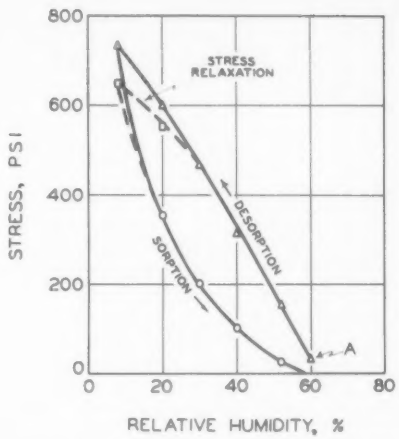

Fig. 9. The tensile stress exerted by an unsupported, processed Kodalith emulsion at constant strain during desorption and sorption of moisture at 70°F. (Replot of data from Fig. 8.) A — Initial stress of 25 psi applied by tensile machine at 60% RH.

to the dimensional hysteresis obtained with the unsupported emulsion after relaxation (Fig. 5).

An attempt has been made to explain this "reversed" dimensional hysteresis exhibited by gelatin-coated films on moisture-resistant supports. Although high polymers exhibit a stress-strain hysteresis,[11] the direction is the opposite from that needed to explain this phenomenon. The magnitude of the base compression at 10% RH (about 0.1%) is very small compared to the emulsion stretch (about 2%). This indicates that the gelatin is the more likely cause of this behavior.

An experiment was devised in which a specimen of unsupported, processed Kodalith emulsion was placed in the jaws of the Instron tensile machine at 70°F–60% RH and subjected to a small tensile stress (25 psi). The relative humidity was then gradually lowered to 10% RH, in steps of 10% RH, allowing 20 min at each step, and then gradually returned to 60% RH in the same way. The jaws of the machine remained stationary during the experiment and the change in stress was recorded automatically through the strain gage. The internal stress in the gelatin during desorption and sorption is plotted against time in Fig. 8, and against relative humidity in Fig. 9. It is clear from these curves that the stress in the gelatin increases in a fairly linear manner as the humidity decreases to about 20% RH. At this humidity or lower the stress is high enough that stress relaxation with time becomes apparent. On the sorption half of the cycle, the stress in the gelatin decreases very much faster than it increased during desorption. This produces a reversed hysteresis loop which is perfectly analogous to the reversed dimentional hysteresis loop of the supported film (Fig 10).

Figures 8 and 9 clearly show that the reversed hysteresis effect is a property associated with the gelatin under tension. It is also apparent that stress relaxation occurs in the gelatin when under tension at low relative humidity. It is likely that greater stress relaxation took place in this experiment than was observed because two opposing effects occur simultaneously when the relative humidity is lowered, i.e., increase in tension and increase in relaxation. Thus a considerable part of this phenomenon can be explained

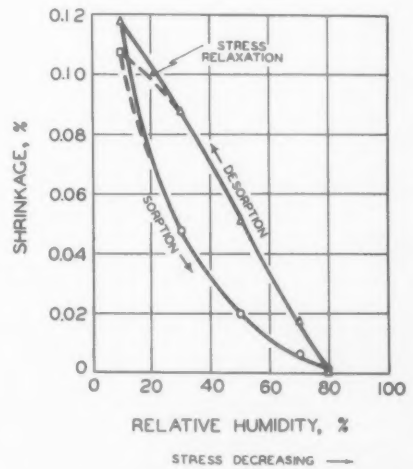

Fig. 10. The shrinkage of processed Kodalith Ortho PB Film upon desorption and sorption of moisture at 70°F. (Replot of data from second cycle of Fig. 7.)

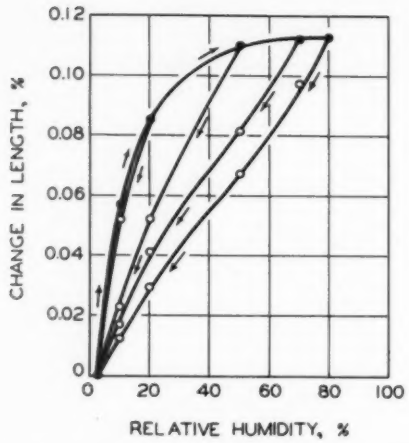

Fig. 11. Effect of various humidity cycles on the dimensional change of processed Kodalith Ortho PB Film, Type 2, at 70°F.

by stress relaxation in the gelatin, although some other factor may also be involved. This reversed dimensional hysteresis has been found with all gelatin-coated polystyrene or other moisture-resistant high polymer supports which were studied. However, the dimensional hysteresis for cellulose-acetate-base films is generally normal in that the sorption curve falls below the desorption curve. This is undoubtedly because acetate base itself absorbs moisture and exhibits a normal hysteresis, which masks the effect of the gelatin.

The practical significance of hysteresis in gelatin-coated films will also depend on the range of relative humidity to which the film is subjected. Figure 11 illustrates various dimensional hysteresis loops in which the spread between sorption and desorption curves varies with the humidity range.

Humidity Coefficients

The hysteresis curves for supported film described in the preceding section illustrate the problem of determining the humidity coefficients of linear expansion. The dimension versus humidity curves are not truly linear; their slopes vary with the previous moisture history, and relaxation of the gelatin interferes above 70% RH (sometimes above 60% RH). Arbitrarily we have chosen to calculate humidity coefficients from the sorption curve between 10% and 60% or 70% RH. Ideally both humidities should be approached from the same side, but in the present work it was more convenient to approach 10% RH from above and 60% or 70% RH from below. Although this makes a small difference in the result, the data are all comparable.

The humidity coefficients of linear expansion of several production polystyrene base films determined in this way are given in Table III. These data show that the thicker base and the thinner emulsion give the lower humidity coefficient. The coefficients also decrease on processing, and decrease slightly more when the film is processed clear than when it is processed black. This is due to the decrease in modulus (Table II) and thickness of the emulsion upon processing.

TABLE III

Average Humidity Coefficients of Expansion of Several Polystyrene Base Films at 70°F

Film	Average measured thickness, mils: Emulsion	Backing	Gelatin-to-base thickness ratio	Humidity coefficient of expansion 10^{-6} in./in./1% RH
Kodalith Ortho PB Film, Type 2 (5-mil base)				
Unprocessed	0.32	0.28	0.120	1.85
Processed black	0.28	0.27	0.110	1.35
Processed clear	0.27	0.27	0.108	1.15
Kodalith Ortho PB Film, Type 3 (5-mil base)				
Unprocessed	0.26	0.24	0.100	1.75
Processed black	0.23	0.23	0.092	1.10
Processed clear	0.23	0.23	0.092	0.95
Kodalith Ortho PB Film, Type 3 (10-mil base)				
Unprocessed	0.26	0.22	0.048	0.95
Processed black	0.24	0.22	0 046	0.60
Processed clear	0.22	0.22	0.044	0.55
Kodak Commercial PB Film, (10-mil base)				
Unprocessed	0.68	0.69	0.137	2.70
Processed black	0.64	0.66	0.130	1.95
Processed clear	0.64	0.66	0.130	1.60

Coefficients calculated between 10% and 70% RH, except for unprocessed Commercial PB Film which was calculated between 10% and 60% RH because of relaxation shrinkage above 60% RH.

The effect of Kodalith emulsion thickness and backing thickness on the humidity coefficient was explored over a wide range in a series of experimental coatings on polystyrene base. As noted by Umberger,[3] the humidity coefficient of photographic film, to a first approximation, is directly proportional to the gelatin thickness and inversely proportional to the base thickness. The data for Kodalith film are plotted in this way in Fig. 12 for unprocessed and processed film and do approximate a linear relationship. The slopes of these curves correlate with the moduli of the emulsion. (For comparison purposes it may be noted that production Kodalith Ortho PB Film has a gelatin/base thickness ratio close to 0.1.)

An equation relating the humidity coefficient of the film to the thickness, modulus, and humidity coefficient of the emulsion and base layers has been derived by Umberger.[3] Umberger did not determine the humidity coefficient of gelatin or emulsion experi-

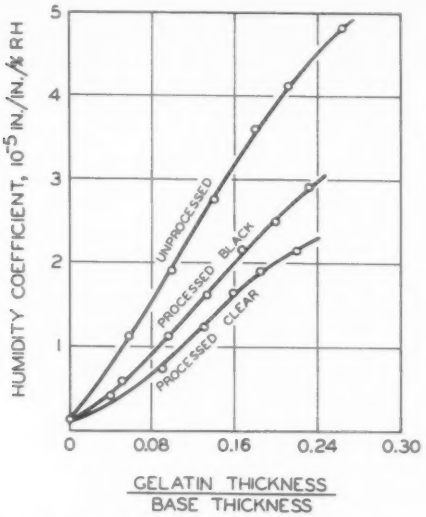

Fig. 12. Effect of gelatin/base thickness ratio on the humidity expansion of experimentally coated Kodalith PB Films at 70°F.

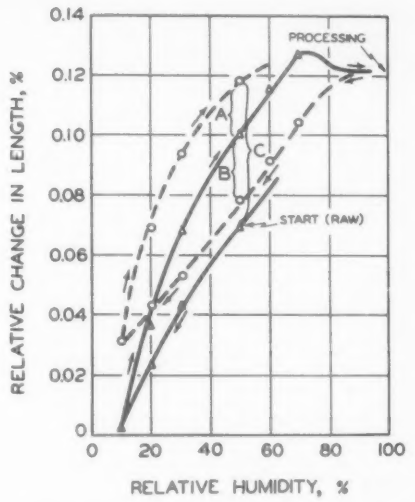

Fig. 13. Dimensional change of Kodalith Ortho PB Film, Type 2, followed through a humidity cycle before processing and again after processing to illustrate how the processing dimensional change depends on the conditioning procedure. The identifying letters correspond to the test procedures listed in Table IV. Solid lines indicate unprocessed (raw) film; broken lines indicate the same film after processing.

mentally but calculated this value from measurements on supported films by means of his equation, obtaining 1.4×10^{-4} in./in./1% RH. Experimental values of this constant determined in the present work for several types of unsupported emulsion and gelatin backings are close to 4×10^{-4} in./in./1% RH (Table I), which is about three times Umberger's value.

This discrepancy is due to the conditions under which the humidity coefficients were measured; other conditions can give results much closer to those calculated by Umberger. Apparently, the *effective* humidity coefficient of the emulsion when attached to the base is appreciably less than the values determined on the unsupported emulsion for Table I. Evidence for this has been obtained by measuring the instantaneous shrinkage which occurs in the emulsion when stripped from a temporary base after equilibration at low relative humidity. This shrinkage is considerably less than the humidity contraction of the unsupported emulsion.

The Umberger equation does not take into account the fact that both the emulsion and base components of photographic film are not perfectly elastic but exhibit stress relaxation and creep under load. For this reason, modulus values used in the equation should be determined at much lower rates of strain than those normally used in tensile testing. At a rate of strain corresponding to that which occurs in film when subjected to humidity changes, unsupported gelatin layers have a modulus of about half the magnitude of those shown in Table II.

Recent data indicate that film having gelatin on one side only has a higher humidity coefficient than film having the same gelatin thickness divided between the two sides. No explanation can be offered for this at the present time.

Regardless of these factors, the Umberger equation is very useful in relating the pertinent variables and predicting their effects on the humidity coefficient of expansion of photographic film.

Processing Dimensional Change

It has been customary in this laboratory for a number of years to measure the processing dimensional change of photographic film by conditioning samples at 50% RH for measurement before processing and again after processing. The conditioning humidity was always approached from below to eliminate any hysteresis effect. This test procedure generally gives a processing dimensional change for polystyrene base film close to zero. Investigation showed that if the film is subjected to a different moisture history prior to conditioning at 50% RH either before or after processing, a slightly different value for the processing dimensional change is obtained. It was apparent that a preconditioning procedure designed to eliminate hysteresis in laboratory tests may be misleading to the film user who takes no such precautions.

The dimensions of an emulsion-coated film sample were followed through a complete humidity cycle before processing and again after processing, and these results are shown in Fig. 13. The hysteresis cycle for the processed film falls above that for the unprocessed film. This is because the modulus and thickness of the emulsion decrease as the result of processing, and this lowers the humidity coefficient of expansion of the film (see Tables II and III). It is clear from Fig. 13 that the processing dimensional change, as measured at any given relative humidity such as 50%, will depend on whether equilibrium is approached from

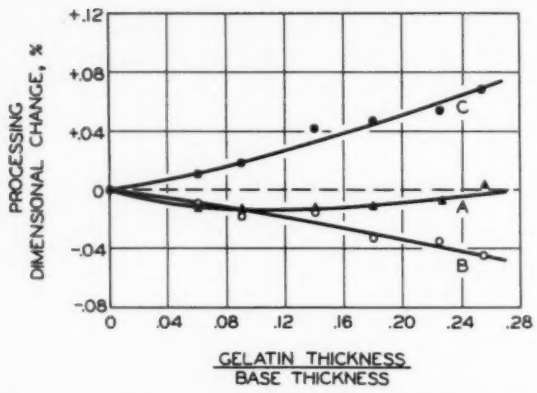

Fig. 14. Effect of gelatin/base thickness ratio on the processing dimensional change of experimentally coated Kodalith PB Films. Letters refer to conditioning procedures in Table IV.

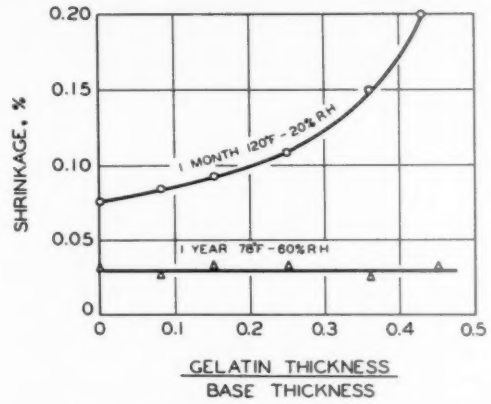

Fig. 15. Effect of emulsion/base thickness ratio on the aging shrinkage of processed, experimental Commercial PB Films. All measurements made after reconditioning to 70°F–50% RH and calculated from an original measurement made before processing.

above or below, both before and after processing. In other words, it depends on the previous moisture history of the film, regardless of the fact that it is conditioned at 50% RH for both measurements.

Four different combinations of preconditioning history before and after processing are possible:

Preconditioning Relative Humidity	
Before processing	After processing
low	low
low	high
high	low
high	high

Three of these combinations are illustrated in Fig. 13 and Table IV. Procedure A gives a processing dimensional change very close to zero; Procedure B gives a small negative value; and Procedure C gives a small positive value. The values for processing dimensional change also vary with the conditioning humidity. It it thus apparent that in commercial practice the processing dimensional change can vary with the weather and the drying procedure. Overdrying after processing or low ambient relative humidities will tend to give a positive processing dimensional change.

The effect of emulsion thickness on the processing dimensional change was investigated with some special coatings of Kodalith emulsion and gelatin backing on 5-mil polystyrene base (Fig. 14). A sufficient range of thickness was used in order to exaggerate the effect. The processing dimensional change increases with the gelatin/base thickness ratio, particularly when determined by Procedure C of Table IV.

Aging Shrinkage

Film base, like all thermoplastics, flows or creeps when subjected to stress for any length of time. It is obvious, therefore, that the lateral compressive force

TABLE IV

Effect of Various Preconditioning Procedures on the Average Processing Dimensional Change of Several Polystyrene Base Films

(All measurements made after reconditioning at 70°F–50% RH)

			Processing dimensional change, %		
			Procedure A	Procedure B	Procedure C
Preconditioning RH of unprocessed film, %			10	10	80
Preconditioning RH of processed film, %			10	*	10
Film Type	Base thickness, mils	Gelatin-to-base thickness ratio			
Kodalith Ortho PB Film, Type 2	5	0.120	+0.01 to −0.01	−0.040	+0.030
Kodalith Ortho PB Film, Type 3	5	0.100	+0.01 to −0.01	−0.035	+0.025
Kodalith Ortho PB Film, Type 3	10	0.048	+0.01 to −0.01	−0.015	+0.015
Kodak Commercial PB Film	10	0.137	+0.01 to −0.01	−0.050	+0.020

* Dried down from a wet condition after processing.

exerted by the emulsion and gelatin backing on the base will cause a permanent shrinkage. It is also clear that the amount of this shrinkage will increase with the following factors:

(1) Increase in thickness of emulsion and backing.
(2) Decrease in storage relative humidity.
(3) Increase in storage temperature.

The first two of these factors increase the compressive stress on the base and the third decreases the modulus of the base, i.e., its resistance to deformation. Some of these effects are illustrated in Fig. 15 which shows that aging shrinkage increases appreciably with the gelatin/base thickness ratio when the film is stored at 120°F-20% RH. However, no such effect is apparent in even a year at 78°F-60% RH, because at this condition the gelatin exerts very little compressive force on the base. (Of course, any shrinkage caused by the emulsion and backing is over and above that which the base alone may show under the same storage conditions.) Although this type of shrinkage is very small with polystyrene-base films under normal storage conditions, Fig. 15 emphasizes the desirability of avoiding storage at very low relative humidities or elevated temperatures in cases where accurate size holding is required over a long period of time.

Conclusions

It has been shown that the dimensional change characteristics of moisture-resistant high polymer base films are highly dependent on the emulsion and gelatin backing employed. The elastic modulus, humidity expansion, and thickness of each layer affect the dimensional response of the film to relative humidity changes, to photographic processing, and to aging effects. Several dimensional change phenomena which occur in the film can be explained in terms of hysteresis, moisture relaxation, and stress relaxation of the gelatin layers An understanding of the phenomena described should assist in controlling or selecting conditions which will minimize the dimensional changes of film in use.

Acknowledgment

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Physical-Chemical Classification of Photographic Developing Agents

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Of the various common photographic developing agents such as hydroquinone, pyrogallol, p-phenylenediamines, Metol, Phenidone,* and mixtures thereof, no two are identical in their reduction of exposed silver halide grains. The differences of practical significance may be accounted for by three qualitative rules: Rule I—proton loss precedes electron loss for active developing agents; Rule II—electron loss should produce a resonance-stabilized free radical for active developing agents; and Rule III—developing agents readily losing two electrons per molecule tend to be catalyzed by oxidants. The rules are consistent with basic physical-chemical principles and with the published experimental observations.

This basic organization of the classic developing agents becomes possible at this time due to application of the principles of the chemistry of free radicals.

Development of the photographic latent image is an oxidation-reduction reaction of considerable commercial importance and theoretical interest. Michaelis'[1] original hypothesis that transfer of electrons from reductant to oxidant occurs one electron at a time has been confirmed in several organic systems by electron spin resonance studies,[2] and one must conclude that radicals or compounds with an odd number of electrons probably are formed during reduction of silver halide by organic developing agents. Thus it has been judged appropriate to apply the principles of free radicals, already established in diverse fields such as biological systems and addition polymerization, to the possible further[3] clarification of development mechanisms. As a result of these studies of the existing experimental data, three qualitative rules have emerged which appear significant because they can account for many of the specific characteristics of the common organic developing agents and can predict the development properties of intermediates such as semiquinone radicals.

Rule I. Proton Loss Precedes Electron Loss for Active Developing Agents

This qualitative rule, which appears fairly obvious from the activating effect of high pH on developing agents, also appears reasonable from the viewpoint of simple electrostatics. Less energy is required to remove an electron from an anion (developing agent less a proton or hydrogen ion) than from a neutral molecule as shown in Fig. 1. Neutral amino developing agents such as phenylenediamines appear to be exceptions to this rule, but their slow action, in spite of favorable penetration of the negative "charge barrier"[3b] surrounding silver halide grains, indicates the approximate correctness of the rule.* Amidol,

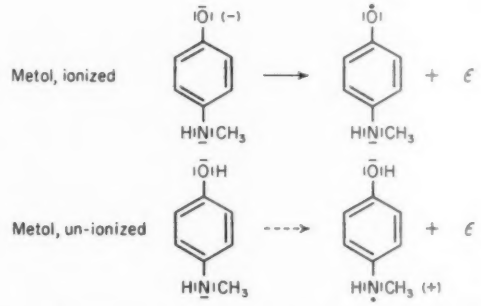

Fig. 1. Rule I — Proton loss precedes electron loss for active developing agents.

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* Phenidone is a registered trade mark of Ilford Ltd. for 1-phenyl-3-pyrazolidone.

* The application of Rule I to phenylenediamines and related compounds is complicated by various factors, e.g., the known solvent action of the amines on silver halides. Also, when a number of strong electron-donor groups such as amino groups are arranged in ortho and/or para configurations in a benzene ring, the reinforced electron donor or reducing power becomes great enough to permit fairly active development by the neutral molecule. Examples of this are compounds with three electron donors per molecule, viz., certain 1,3,4-triaminobenzenes and "Amidol," 2,4-diaminophenol. Also the presence of electron donor groups in such abundance should provide additional stable resonance isomers of the free radical with lower development activation energy and more active development by Rule II.

2,4-diaminophenol, increases in reducing action with increasing degree of ionization.

An interesting conclusion from Rule I is that Metol, which because of its N-methyl-*p*-aminophenol structure has only one proton ionizable at normal developer pH, would readily lose only one electron; Metol resembles Phenidone in this respect. Hydroquinone, with two phenolic groups, differs from Metol in that it can readily lose two protons and thus two electrons. This would seem to be advantageous, but, by itself, hydroquinone is a relatively inactive developing agent for reasons which will become clear in the next section.

Rule II. Electron Loss Should Produce a Resonance-Stabilized Free Radical for Active Developing Agents

Electron transfer from a reductant to an oxidant normally occurs one electron at a time. The free radical formed by loss of one electron from an active developing agent must be a relatively probable structure so that its formation is not prohibited by the requirement of excessive activation energy. Michaelis[1] has shown that semiquinone and related free radicals of significance must be stabilized by resonance between likely mesomeric structures. Such resonance favors the formation of free radicals via minimization of energy and delocalization of the odd electron; in a sense the energy "saved" by resonance in the free radical is "spent" or used to split the coupled electron pair in the original developer molecule.

Making use of Rule II, it appears that doubly ionized hydroquinone is able to transfer the first electron because the semiquinone so formed is stabilized by strong resonance between identical structures shown in Fig. 2.

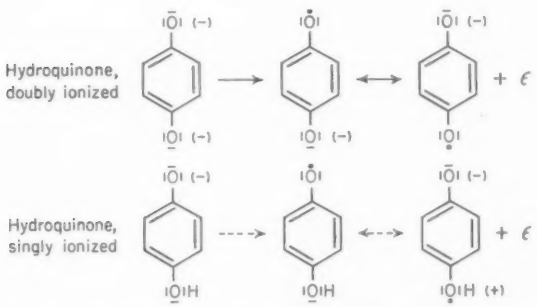

Fig. 2. Rule II — Electron loss produces resonance-stabilized free radical for active developing agents.

It appears that singly ionized hydroquinone, though able to penetrate the charge barrier, should be a weak developing agent due to relative inability to transfer the first electron; the semiquinone so formed is subject to weak resonance between unlike structures, one of which is improbable because of the energy required to separate plus and minus charges in the structure. Doubly ionized hydroquinone, though able to transfer electrons readily, appears limited as a developing agent by slow penetration of the negative charge barrier surrounding the silver halide grains and by the requirement of excessively high pH for double ionization.

However, in developers such as catechol and pyro, which contain ortho phenolic groups, the singly ionized forms are capable of development.[4] A form of hydrogen bonding between the ortho groups appears to stabilize the semiquinone of the singly ionized material, the shared proton making the resonance forms of the free radical essentially equivalent.

Singly ionized Metol should be able to lose the first electron because the resulting free radical is stabilized by resonance. Though the two end groups are different (Fig. 1), the free radical resonance isomers have roughly equal energy, because in polar solvents the neutral amino group is roughly equal to the ionized phenolic group as an electron donor[5] as witnessed by resonance in merocyanine sensitizing dyes. Thus Metol qualifies as an active single-component developing agent since it can both penetrate the charge barrier and readily transfer an electron in its singly ionized form.

Rule III. Developing Agents Readily Losing Two Electrons per Molecule Tend to Be Catalyzed by Oxidants

By Rules I and II, hydroquinone can lose two electrons, i.e., its semiquinone ion should be a good developer; thus oxidants could catalyze hydroquinone development via production of relatively large amounts of semiquinone ion (Fig. 3), which because of its single negative charge and more efficient charge barrier penetration is faster acting than the doubly charged ion. By the same rules neutral Metol semiquinonimine should be a poor developer; thus oxidants could possibly retard Metol development via destruction of the active Metol to form the relatively inactive semiquinonimine. Phenidone should behave like Metol in this respect.

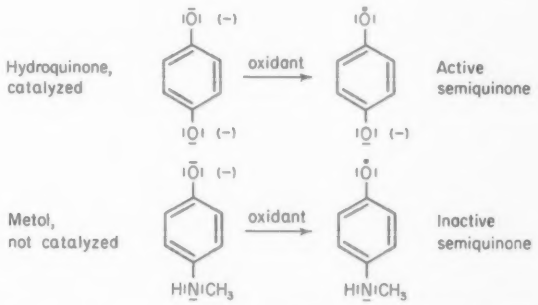

Fig. 3. Rule III — Developing agents readily losing two electrons per molecule tend to be catalyzed by oxidants.

The effect of oxidants in catalyzing hydroquinone development is well known.[6] Metol development is reportedly somewhat retarded by oxidants. There is experimental evidence[7] that quinone is specifically adsorbed to the surface of the silver halide grains.* Diffusion of hydroquinone to the grain surface would occur with subsequent reaction with adsorbed quinone to form an active concentration of semiquinone ion in excess of that in equilibrium with the main body of developer. Molecular oxygen, with its two unpaired electrons, could be adsorbed to the metallic speck comprising the latent image and thus could aid formation of active semiquinone ion, ready for development, at the surface of the silver halide grains.

Discussion

It is of interest to discuss the further application of the proposed rules, firstly, to the well-known classes of developing agents and their development kinetics; secondly, to mixtures of developing agents which are in common use; and finally, to the theory of the latent image.

Dihydroxy-, Hydroxyamino-, and Diamino-Benzene Developing Agents

It appears from the above rules that the active species of a developing agent should preferably be an anion in its developing solution and should be capable of forming a stable species by loss of one electron.

For hydroquinone, we thus can eliminate all except the doubly ionized form and the semiquinone ion (Fig. 4) as active species. Let us now compare the

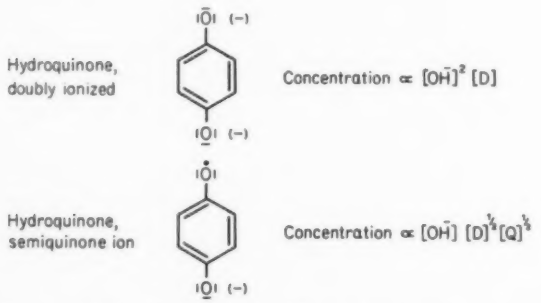

Fig. 4. Probable active developing forms of hydroquinone.

development kinetics that should result from these two active species.

It is reasonable to assume that the rate of production of silver density is a function of the concentration of active developing species. By the use of the usual ionization equilibrium expressions, it is found that the concentration of the doubly ionized form of hydroquinone is proportional, in the pH range 8 to 9, to $[OH^-]^2\,[D]$, where $[D]$ is the total concentration of hydroquinone added to the solution. By combination of the hydroquinone ionization and the semiquinone dismutation equilibria, it is found that the concentration of the semiquinone ion is proportional to $[OH^-][D]^{1/2}[Q]^{1/2}$, where $[Q]$ is the concentration of the oxidized form, quinone, in the developer. The observed[8] dependence of developing rate is on the first power of hydroxyl ion and the one-half power of the hydroquinone concentration under some conditions. The occurrence of the factor $[Q]^{1/2}$ in the expression for semiquinone concentration is in the right direction for explaining quinone catalysis, but quantitatively it is in disagreement with existing data. Probably the semiquinone acts in the early stages to shorten the hydroquinone induction period, the doubly ionized form taking over when the negative charge barrier is broken. In addition, the development rate appears complicated by grain-adsorption phenomena.

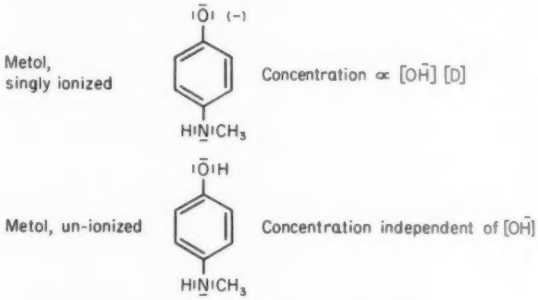

Fig. 5. Probable active developing forms of Metol.

For Metol (Fig. 5) all structures except the singly ionized form can be eliminated from consideration as strongly active species at normal pH. The concentration of this species is proportional to $[OH^-][D]$. At low pH, the relatively pH-insensitive development observed for Metol is usually ascribed to slow development by the molecular or un-ionized form. At normal pH, development by the singly ionized form predominates as shown by linear dependence on hydroxide concentration under some experimental conditions.

For *p*-phenylenediamine, the most active form indicated by Rules I and II is the semiquinone anion (Fig. 6) — if it is present in any reasonable concentration. Thus at relatively low pH, pH-insensitive and slow development by the molecular species will predominate, but at high pH, the semiquinone anion may occur to produce supplementary development. This can account for the observed pH dependence of these "neutral" developing agents and the observed induction period at high pH (due to the negative

* The apparent adsorption of quinone by exposed silver halide, indicated by Staude's experiments, could be explained as an oxidation of latent image material with the formation of semiquinone, which then remains adsorbed by the silver halide. Unexposed silver halide apparently does not "adsorb" quinone. — *T.H.J.*

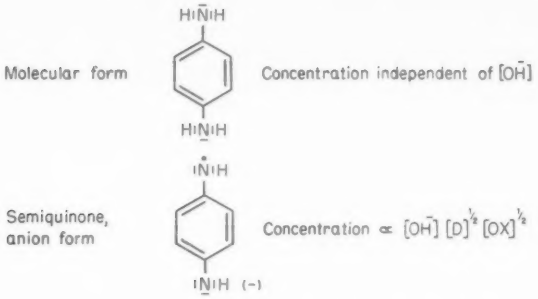

Fig. 6. Probable active developing forms of *p*-phenylenediamine.

charge of the semiquinone anion). However, this would also seem to predict oxygen catalysis at high pH, a phenomenon not yet observed for *p*-phenylenediamine, but the negative-charge barrier retardation would not favor this semiquinone anion as it does that of hydroquinone.

Mixed Developing Agents

Phenidone (or Metol) starts the development in the usual developer mixture with hydroquinone as shown in the top reaction of Fig. 7. By Rule I, Phenidone free radical is a poor developer, i.e., it

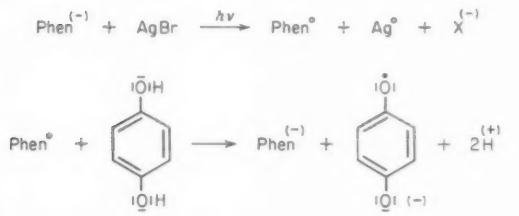

Fig. 7. Mixed developing agents.

will not react with silver halide. Simple test tube experiments show that Phenidone free radical also does not react with sulfite ion but *does* react with hydroquinone, probably to produce the active developer, semiquinone ion, which with its −1 charge penetrates the charge barrier. In other words, Phenidone free radical is formed by the development reaction at the grain surface and there acts as an oxidant to catalyze hydroquinone development. It is hypothesized that this contributes to the observed "superadditivity." Thus, mixed developers (Phenidone or Metol, plus hydroquinone) have not one but probably two active developing agents with favorable short induction periods — Phenidone ion and semiquinone ion — both having a single negative charge. By regeneration mechanism,[9] the concentration of these two active forms is held constant with use at the expense of hydroquinone, which is consumed.

The Free Radical Characteristics of the Developing Latent Image

The latent image for chemical development has usually been assumed to be similar to the metallic structure which catalyzes physical development. For understanding the implications of our proposed development rules to the structure of the latent image, it is helpful to adopt the transition state viewpoint of chemical kinetics.

The following chain of events is proposed for chemical development.

(a) The active developer anion diffuses to the conducting metal speck which is the latent image.

(b) The metal speck is polarized so that the negative field of the developer anion encourages migration of a silver ion (e.g., an interstitial silver ion, an ion moving along an internal or external surface, or, in physical development, a silver ion migrating from the solution) to the negatively polarized end of the speck.

(c) Transition or "critical" complex formation is now completed as shown in Fig. 8. In the critical configuration, this complex can decompose into reactants or products (elementary silver plus oxidized developer), depending on the statistical path of the resonating electrons. The complex is composed of the developer, the latent image, and a silver ion joined by a resonating system of one- and two-electron bonds.

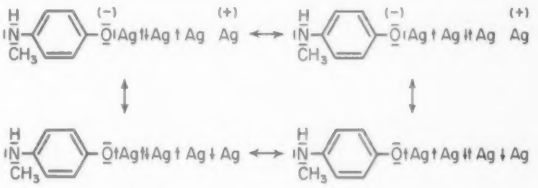

Fig. 8. Activated complex or critical configuration for chemical development.

In Fig. 8 the latent image is represented as three silver atoms in a row, but the most stable structure would probably consist of the silver atoms arranged in a close-packed structure[10] to produce a maximum number of coordinations with near neighbors. Only a few of the resonance isomers are represented in this figure but it can be recognized that the upper resonance configurations represent the reactants and the lower resonance configurations represent the products of the development reaction. Similar structures of the critical complex of chemical development can be drawn for negatively charged developers other than Metol and even for the slower acting neutral developers.

Any free radical nature of the latent image should aid in the uncoupling of the electron pair of the developing agent required to meet the Michaelis condition of transferring electrons one at a time. Thus,

aggregates containing an odd number of silver atoms would be expected to be most paramagnetic and catalytically active. However, metallic crystals in general have one-electron bonds, according to Pauling,[5] and these most probably add to catalytic activity regardless of odd or even structure. Langmuir,[11] in postulating a dissociation into atoms of hydrogen molecules absorbed by metals, was early in recognizing the ability of metal catalysts to uncouple electron-pair bonds.

Considerations of the nature of the metallic bond indicate that two silver atoms cannot exhibit typical metallic properties such as conduction, because the electrons are localized in the bond.[12] However, an aggregate of three or more silver atoms permits electronic delocalization and conduction, and it would seem that the smallest posible latent image would consist of three silver atoms. This would leave the sub-latent image to consist of two silver atoms joined by an electron-pair bond. Such structure should be relatively inactive as a catalyst because of absence of metallic properties.

Electron transfer from the developing anion to internal silver ions is visualized to occur through the medium of the conducting, polarizable metal speck comprising the latent image. From this viewpoint, chemical development is merely an extension of the latent image formation, the developer providing the electrons which during latent image formation are those released into the conduction band by light absorption.

Acknowledgments

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The Role of Silver Bromide Complexes in the Mechanism of Aging Fog

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The effect of emulsion pH and pAg on fog stability under adverse aging conditions has been investigated. The pH was varied from 5.3 to 7.4 and the pAg from 8.7 to 10.5 in factorial experiments using bromo-iodide emulsions. Aging fog increases with increasing pH and is greatest at either high or low pAg, with a pronounced minimum at the intermediate value of 9.9. This minimum is explained quantitatively through the formation and thermal decomposition of the complex $(Br_5Ag)^{-4}$ into silver and bromide ions, the silver ion being fundamental to the fog formation mechanism. The importance of the ionic strength and dielectric constant of the grain environment in relation to the mechanism is discussed.

Coated photographic emulsions are known to undergo changes in fog with storage, especially when stored under adverse conditions of high temperature. The effect of emulsion pH and pAg on aging fog has been reported earlier by Carroll, Hubbard, and Kretchman.[1] The objective of this work was to extend the investigation of those variables with the hope of gaining further knowledge of the aging fog mechanism.

Experimental Procedure

The emulsions used in this investigation were prepared from ammonia-ripened bromo-iodide (1.7 mole % iodide) precipitation employing a lime-processed bone gelatin. They were chemically sensitized without either optical sensitizing or antifogging adjuvants and were identical except for the pH and pAg of the liquid emulsion at 35°C. The pH and pAg values refer to the quantities measured in the liquid emulsion prior to coating. As it is difficult to apply reversible thermodynamics to a solid film, no attempt has been made to relate these values with probable values of pH and pAg in the coated layer. Emulsion pH was adjusted with either sulfuric acid or sodium hydroxide and measured with an electrometer using a glass electrode and a saturated calomel reference electrode. The pAg was adjusted with calculated quantities of potassium bromide and checked potentiometrically. The amount of bromide to be added for a given pAg was determined by a potentiometric titration of the emulsion, using a silver electrode and a calomel reference electrode at 35°C. To insure reproducibility the silver electrode was carefully conditioned prior to the titration by polishing with a detergent containing a fine abrasive and soaking for 24 hours in 3 N silver nitrate; the electrode was permitted to equilibrate for at least 30 min in the emulsion before the potential was read. The pAg values at equilibrium were calculated from the measured potential and the standard half-cell potentials of the silver electrode and the saturated calomel cell. The potential used for $Ag = Ag^+ + e$ was -0.7891 as determined by Owen and Brinkly[2] and for the calomel cell was -0.2339 from Hamer.[3] It has been estimated that the maximum possible error for the measured pH values is ± 0.05 and for the pAg values ± 0.10.

The emulsions were coated on cellulose acetate film base at 35°C and immediately chilled and set at 7°C. Drying was for a period of about 2 hours at dry and wet bulb temperatures of approximately 30°C and 20°C respectively. The coating weight of silver halide on film base was 1 mg/sq cm ± 2%.

To accelerate fog instability, aging was carried out by storing 35mm strips in total darkness for seven days at the relatively high temperature of 52°C and 65% RH. After storage, the emulsions were conditioned at 21°C and 50% RH for 24 hours before processing. A Metol-hydroquinone developer of the following composition was used with constant agitation at 20°C for 5 min:

3.0	grams Metol
9.0	grams hydroquinone
50.0	grams Na_2SO_3
50.0	grams K_2CO_3
4.5	grams KBr
	Water to make 1 liter

Diffuse visual fog densities were measured on laboratory densitometers to a maximum density of 3.00.

Experimental Results

Two separate sets of emulsions were made in which pH was varied from 5.3 to 7.4 and pAg from 8.7 to 10.5

Presented at the Annual Conference, Rochester, N.Y., 9 October 1958. Received 12 September 1958.

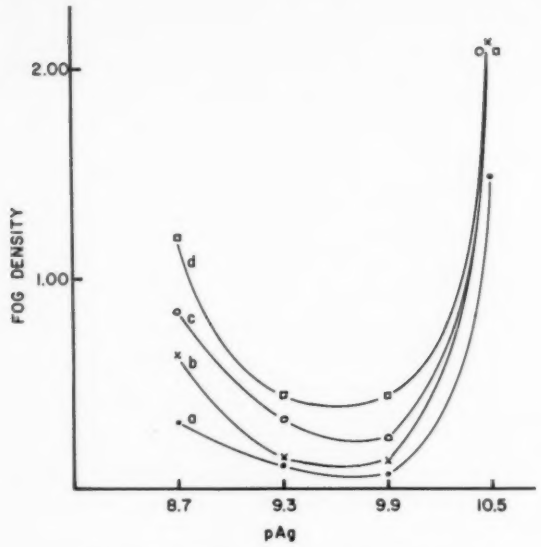

Fig. 1. Aging fog as a function of emulsion pAg and pH.
Curve a — aging fog at emulsion pH 5.3.
Curve b — aging fog at emulsion pH 6.0.
Curve c — aging fog at emulsion pH 6.7.
Curve d — aging fog at emulsion pH 7.4.

TABLE I
Average Aging Fog Data

pAg	pH 5.3	pH 6.0	pH 6.7	pH 7.4
8.7	0.32	0.66	0.85	1.21
9.3	0.11	0.14	0.34	0.44
9.9	0.09	0.13	0.23	0.44
10.5	1.45	2.11	2.10	2.10

in a 4 × 4 factorial design.[4] Fresh fog values were uniform at 0.11 ± 0.02 for both sets of emulsions. The high temperature aging test was performed twice for each set. Results from all four tests were averaged and are given in Table I and plotted in Fig. 1. Aging fog increases with increasing pH and is greatest at either high or low pAg with a pronounced minimum at the intermediate value of approximately 9.9.

To determine the reliability of the data and the significance of the fog minimum at the emulsion pAg of 9.9, an analysis of variance[4] was carried out on all 64 experimental points. The results of the analysis are given in Table II. The F values which are given refer to the ratio of the "mean square" of the experimental data for the various factors (pH, pAg and the interaction of pH × pAg) to the "mean square for error." They are compared to the F values required for a factor to be considered significant with a given confidence. When we refer to a factor as being significant at the 1% or 10% levels, we consider it to be significant with 99% or 90% confidence respectively.

TABLE II
Results of the Analysis of Variance of the Aging Fog Data

Factor	Degrees of freedom	F required for significance at the level 25%	10%	5%	1%	F Experimental
pAg	3	1.41	2.20	2.80	5.00	23.97
pH	3	1.41	2.20	2.80	5.80	2.30
pH × pAg	9	1.32	1.76	2.10	2.80	0.23

The analysis indicates that at the 1% level the effect of the emulsion pAg on aging fog was highly significant in relation to the experimental error. Furthermore, while the effect of emulsion pH approaches significance at the 10% level, the two-factor interaction of pH × pAg was found to be insignificant at all levels. A test of the reciprocal of the F value substantiated the non-significance of this interaction. This may be interpreted as meaning that, in the region investigated, the behavior of aging fog with emulsion pAg is independent of the level of emulsion pH. Thus, in a theoretical explanation for the existence of the fog minimum, emulsion pH can be ignored.

Discussion

This same pH-pAg region has been extensively investigated for sensitivity, low- and high-intensity reciprocity law failure, and latent image fading; the results have been reported elsewhere.[5] The effect of soluble bromide on stability was investigated by Carroll, Hubbard, and Kretchman[1] up to a pAg value which we estimate to be about 9.7. In none of these responses was a minimum observed with emulsion pAg as was the case with high temperature aging fog. The absence of minima in the aging fog of the varied emulsions reported by Carroll, Hubbard, and Kretchman can be attributed either to the lower pAg region investigated or, as will be shown, to the lower temperature (30°C) used for storage.

The suggested explanation of the aging fog minimum is based on our knowledge of the silver-containing ionic species which exist in equilibrium over this pAg range and which could supply silver for the fog formation reaction. The importance of the silver–gelatin complex is recognized in the photographic process[6] and particularly in aging phenomena.[1,7] These complexes are known to be highly pH sensitive and, as the minimum in fog has been shown to be independent of emulsion pH, they need not be considered here. The silver-bromide complexes, however, should be considered.

Erber[8] and Chateau and Pouradier[9] established potentiometrically the existence of the complex ions $(Br_3Ag)^{-2}$ and $(Br_5Ag)^{-4}$ in dilute solutions of silver nitrate and potassium bromide. Pouradier, Venet, and Chateau[10] also found the $(Br_5Ag)^{-4}$ ion to predominate at increasing concentration. Assuming the activity coefficient of the bromide complex to be equal to that of the bromide ion at a given concentration, they calculated values for the dissociation

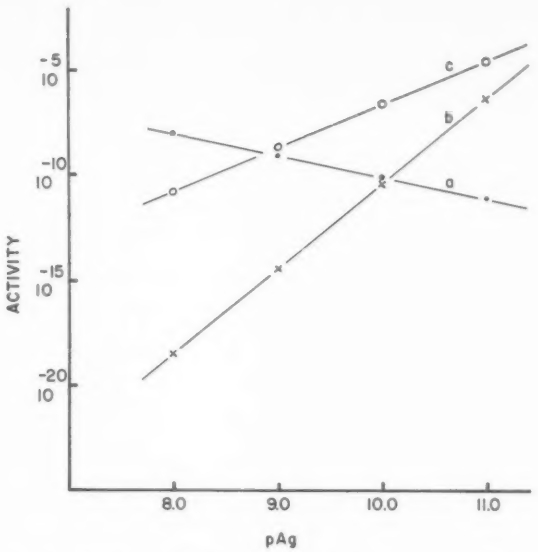

Fig. 2. Activities of the silver-containing ionic species in equilibrium with silver bromide at 35°C as a function of pAg.
Curve a — activity of Ag^+.
Curve b — activity of $(Br_5Ag)^{-4}$.
Curve c — activity of $(Br_3Ag)^{-2}$.

constants of these two complexes as a function of temperature and gave the equations:

$$\log K_{3-1} = \frac{-2767}{T} + 0.424$$

$$\log K_{5-1} = \frac{-4450}{T} + 5.830$$

where T is the absolute temperature and K is the mass action constant. The constant for this equilibrium is written as

$$K_{mn} = \frac{[\gamma_{Br}(Br^-)]^m\,[Ag^+]^n}{\gamma_c\,(Br_mAg_n)}$$

The terms (Br^-), (Br_mAg_n), and $[Ag^+]$ refer to the concentration of free Br^- ions, complex ions, and the activity of the silver ions. The terms γ_{Br} and γ_c are the activity coefficients of the bromide ions and the complex ions.

With additional information regarding the solubility product of the silver halide crystals the activities of these complex ions were calculated for the photographic pAg range 8 to 11. The solubility product used for these calculations was that of silver bromide. As the iodide distribution for the cyrstals was not known and as the most soluble grains in the system control the ionic equilibrium, this simple model was chosen. The value of the solubility product at the coating temperature of 35°C is 11.8, as given by Owen and Brinkly.[2] The value used for K_{5-1} at 35°C was 2.41×10^{-9} and for K_{3-1} was 2.76×10^{-9}. The results of these calculations are given in Table III.

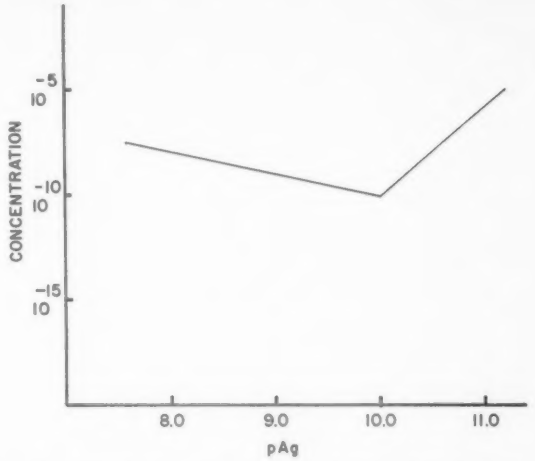

Fig. 3. Approximate total concentration of Ag^+ and $(Br_5Ag)^{-4}$ ions as a function of emulsion pAg.

TABLE III
The Activities of Silver Bromide Complexes in Equilibrium with Silver Bromide at 35°C as a Function of pAg

	pAg			
Ion	8.0	9.0	10.0	11.0
$(Br_3Ag)^{-2}$	1.4×10^{-11}	1.4×10^{-9}	1.4×10^{-7}	1.4×10^{-5}
$(Br_5Ag)^{-4}$	4×10^{-19}	4×10^{-15}	4×10^{-11}	4×10^{-7}

The activities of the silver-containing ionic species are plotted as a function of pAg in Fig. 2. If it is assumed that a coated photographic emulsion would be representative of the more concentated solutions described by Pouradier, Venet, and Chateau[10] because of its high ionic strength, and that no ions richer in Br than those found by these authors are formed, the predominant complex in the system would be $(Br_5Ag)^{-4}$. Adding Curves (a) and (b) of Fig. 2, a new curve is obtained which represents the total of the activities of the ions in the grain environment capable of furnishing silver to a given reaction. This curve, which is also an approximation of the total concentration of the ions, is given in Fig. 3. There is a distinct minimum at a pAg of 10.0. The correspondence of this minimum and the minimum observed for aging fog is within experimental error.

It was hypothesized by Carroll, Hubbard, and Kretchman[1] that aging fog is due to a continuation of chemical ripening. As extended chemical ripening has been claimed to produce silver specks,[11] Smith[7] suggested that a similar behavior occurs during aging of a coated emulsion. The silver ion is fundamental to this mechanism. Thus it would be anticipated that an increase in fog would occur with the increasing silver ion concentration at pAg values below 10.0. It also appears quite plausible that under high temperature aging conditions, the complex $(Br_5Ag)^{-4}$, which is in

abundance at pAg values greater than 10.0 and which is known to be more thermally unstable than the $(Br_3Ag)^{-2}$ complex,[10] could furnish silver to the fog reaction, each complex ion furnishing one silver ion. The data of this experiment are thus consistent with the aging mechanism proposed by Carroll, Hubbard, and Kretchman, and expanded by Smith.

In the above discussion there were two reasons given for the greater role played in the aging fog mechanism by the $(Br_5Ag)^{-4}$ than the $(Br_3Ag)^{-2}$ complex – its higher thermal instability and its predominance at increasing concentration. This phenomenon of one ionic species being formed preferentially over another as a function of the solution concentration can be thought of as being influenced by the ionic strength (Lewis and Randall) of the system. Ionic strength is known not only to affect the activity coefficients of ions (Debye-Hückel) but also the rate at which ionic equilibrium is reached (Brönsted-Bjerrum). If aging fog and other photographic properties are largely dependent on the establishment of specific complexes in the emulsion during chemical ripening and drying, ionic strength should have great effect and should be considered in the formulation of mechanisms of the photographic process. It should be mentioned that the above relationships involving ionic strength are derived for media of constant dielectric constant. As it is quite conceivable that the constants for gelatin in solution and when dried are quite different, the dielectric constant would play an even greater role than ionic strength *per se*.

Summary and Conclusions

The results of factorial experiments of emulsion pH and pAg have indicated a minimum in aging fog to occur at a pAg of 9.9. This minimum is independent of emulsion pH and can be explained through the formation and thermal decomposition of the complex $(Br_5Ag)^{-4}$ into silver ion and bromide ions. The data are consistent with an aging fog mechanism involving the formation of specks of silver on the silver halide surface.

Acknowledgment

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A Self-Threading Processor and Dryer for Use with Specific Sheet Films

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A combined self-threading processor and dryer is described in which individual sheets of photographic film are transported from station to station by means of rollers. In the processing section, the transport rollers in contact with the sensitized surface of the film also provide an effective degree of agitation by displacing the solution, rich in reaction products, which is adjacent to the emulsion surface. In the dryer the film continues to be transported by rollers and is dried by high-temperature, high-velocity, air impingement. Although especially adapted for use with films having an emulsion coating on both sides, such as certain x-ray films, the processor is also of interest for use with other sensitized products.

Photographic processors ordinarily may be classified in one of two broad categories, those handling a continuous web, as in the case of the motion-picture film processor, and those handling individual sheets or lengths of photographic material. Specialized designs exist in which a processing machine may be useful in both fields of application, but this is relatively uncommon. Each of the broad categories may be subdivided in several ways, one of the distinctions being between a self-threading and a non-self-threading design. We shall consider here the evolution of a self-threading processor, based on the use of multiple transport rollers, for handling individual sheets of photographic film and shall speculate briefly on its possible application in handling other forms of photographic material.

A review of the photographic literature shows that, over the years, there has been no lack of schemes proposed and models built for transporting individual sheets of photographic materials through the various stages of processing. In recent times, particularly, the various methods for providing rapid duplication of documents by photographic procedures have led to the commercial development of several of these individual sheet, self-threading devices. However, as perf rmance requirements increase, or as the nature of the photosensitive material makes it more difficult to handle, the number of available auto-transport methods diminishes sharply.

One of the more demanding of the film products, as far as processing and handling requirements are concerned, is x-ray film which has the emulsion coated on both sides of the support. In addition to the normal susceptibility of this film to careless handling before processing, which results in abrasion marks, kinks, etc., nonuniformity in density can occur from deficiencies in processing which may affect the certainty of a clinical diagnosis. The fact that such films bear a sensitized emulsion on both sides demands special consideration through both the processing and the drying stages. Under these conditions, most of the film-transport schemes used for other applications fail, so that such films are normally processed either by hand or by a mechanized form of the hand technique. In either case, the films are first loaded in individual hangers which are then transported from tank to tank by hand or by a machine designed to accomplish the same purpose. Agitation to improve uniformity of development is ordinarily relatively mild and consists in moving the film during development, gas-burst agitation, or similar procedures. After washing, the films, which are still in hangers, are drained and dried,

Fig. 1. An over-all view of an X-Omat Processor.

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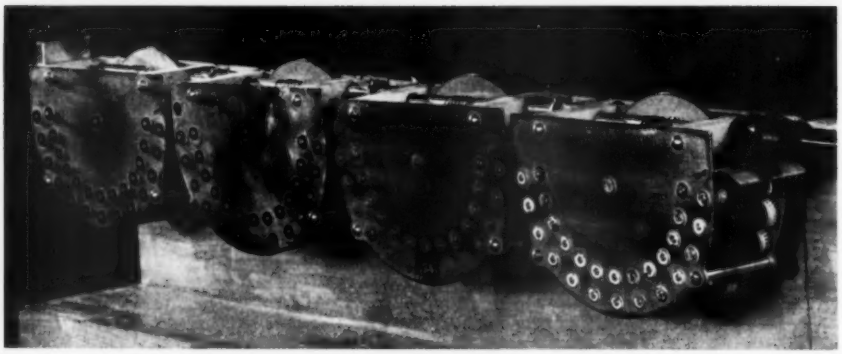

Fig. 2. Experimental roller-transport processor for dental-size x-ray films.

either by forced-air circulation, normally within a drying cabinet, or, with mechanized equipment, they are automatically transported through a hot-air dryer or one equipped with infrared radiators. A normal dry-to-dry processing cycle for a film such as Kodak Blue Brand X-Ray Film is about 1 hour.

The self-threading processing machine to be described in this paper was designed for processing Kodak Royal Blue X-Ray Film and Kodak Blue Brand X-Ray Film although, as will appear later, variations of this design are likely to be useful in processing other types of films. Briefly, from the time the film enters the machine to the time it drops, dried, into the receiving bin, 6 minutes later, it is transported through the various stages of processing and drying by driven transport rollers which establish the film path. A commercially available processor of this type is shown in Fig. 1.

Before describing the film-transport system used in this fully automatic processor, it is desirable to review briefly the several steps leading to its development.

The earliest direct antecedent of the present commercial model was an experimental dental x-ray processor developed in 1950 by H. F. Sherwood of the Kodak Research Laboratories. This unit, shown in Fig. 2, consisted of four stages through which the small-size dental films were transported at the rate of 1 fpm. As shown in Fig. 3, the film passed between pairs of driven rollers arranged in a semicircular pattern. Although the rollers were arranged as wringers, only slight pressure was exerted on the film. The favorable size and stiffness properties of the miniature dental films helped to simplify the transfer of film from station to station by means of a simple deflector plate, as shown at (A) in Fig. 3.

As a result of early work on this processor, it became evident that the roller-transport system provided not only the means for transferring the film from one station to the next, but, in addition, it provided a high degree of agitation which resulted in excellent uniformity of development. As with brush development, in which the reaction products of development which contribute to nonuniformity effects are periodically wiped from the surface of the film by the action of a brush, intermittent and frequent contact of the film with transport rollers produces a similar result.

It may be mentioned here that the versatility of the roller-transport system was further demonstrated at this time by processing continuous lengths of 16mm film on the same equipment.

Because the inherent advantages of this arrangement which combined both the transport function and the agitation function in the same roller mechanism were self-evident, a considerably larger machine, capable of processing 14-in.-wide x-ray film was built in 1953. After a short period of use, it was proposed that one set of transport rollers be offset one-half pitch with respect to the other set, and that the two rows be brought closer together to cause the film to weave slightly as it passed from roller to roller. As shown in Fig. 4, this had the effect of increasing the area of contact between the roller and the film, and helped to insure more positive film transport. All rollers were driven. The cross-over from station to station was achieved by means of curved shoes which directed the leading edge of the film between a pair of

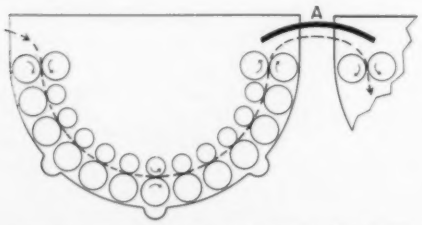

Fig. 3. Arrangement of rollers in experimental roller-transport processor for small-size films.

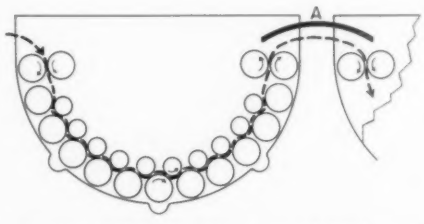

Fig. 4. Staggered-roll system used in experimental processor for large-size films.

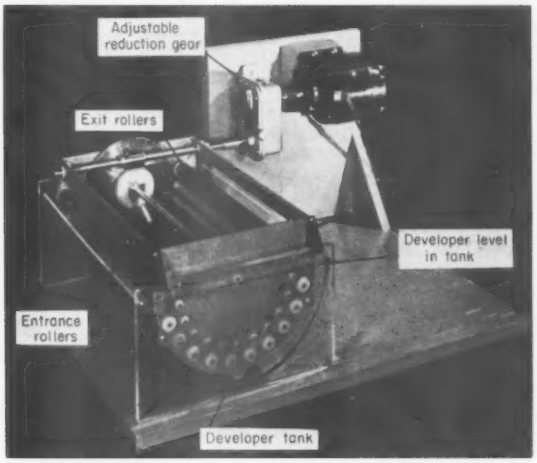

Fig. 5. Experimental roller-transport processor for large-size, cut-sheet film.

rollers at the entrance of each rack. A single rack from this machine, housed in a transparent tank, is shown in Fig. 5.

This particular processor was most useful in the study of the properties of photographic solutions required for roller-transport processing. Because of its unusual capabilities, it also helped to bring into focus the fact that a dryer of uncommon design was required to take advantage of the capabilities of a processor of this type. It will be evident that, as far as the processor was concerned, it was capable of transporting any width sheet film, less than a maximum, and that it could accept these films in random order and position, two or more abreast if space permitted. There was also evidence that, with suitable safeguards, films of substantial length could also be accommodated. Furthermore, since both sides of the film received almost identical treatment, the processing system was ideal for use with duplitized film products.

Dryer for Use with Roller-Transport Processing System

As might be expected, the design and development of a dryer which avoided placing limitations on the versatile processing section presented challenging problems. Although many widely different schemes were investigated, the design ultimately arrived at was one in which the film was transported through the dryer between pairs of relatively closely spaced rollers, thus satisfying all film-size and sequence requirements, and was dried by high-velocity, hot air impingement. It was recognized at the outset that the normal result of such a combination of factors in drying would be that the film might be expected to stick to certain rollers during the course of drying, while severe drying patterns would normally result from the discontinuity in drying, introduced by the presence of the rollers. In truth, these and similar occurrences were characteristic of the results obtained during much of this study. However, with a given film, in this case Kodak Blue Brand X-Ray Film, it was possible to establish a combination of chemical and mechanical conditions in the processor and dryer which permitted attainment of the highest-quality processing. The chemical factors applying to processing on equipment of this type are discussed in a paper by H. D. Russell,* while the essential mechanical features of a roller-transport processor and dryer are dealt with here.

A Roller-Transport, Film-Processing Machine

Since most of the detailed studies applying to roller-transport processing have been conducted on the Kodak X-Omat Processor, Model M, the descriptive material to follow will apply in large part to this equipment.

An understanding of the over-all operation of the X-Omat Processor can be obtained from the cut-away drawing (Fig. 6). The part of this machine to the left of the panel is the film-feed section and this is normally located in a photographic darkroom. The rest of the machine, consisting of the processing section and the dryer, is located in fully illuminated space on the opposite side of the darkroom wall. To prevent light fog, the developer and the stop-bath sections of the processor are shielded by a protective cover.

In normal operation, individual sheets of exposed x-ray film are fed singly, or, if lateral space permits, in

*See page 32, this journal.

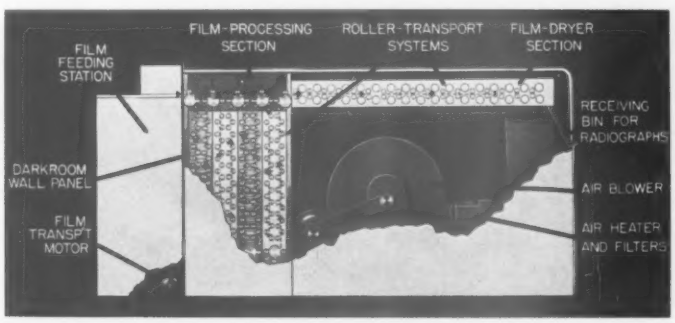

Fig. 6. Cut-away view of interior of X-Omat Model M Processor.

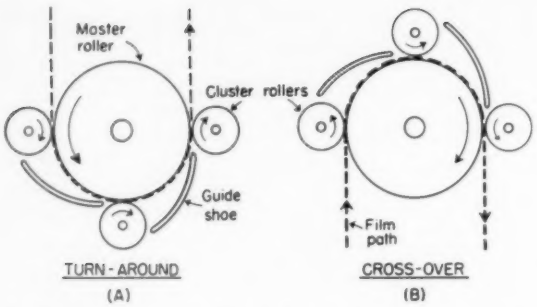

Fig. 7. Arrangement of rollers used to change the direction of film travel.

parallel through a narrow slot in the housing of the feed section. Here it is picked up by rollers which deliver the film to the processing section of the machine where it is accepted by a special grouping of rollers to be described later, which directs the leading edge vertically downward, as shown in Fig. 6. The film is then transported vertically, in this case at the rate of 5 fpm, between driven rollers arranged in staggered positions as shown. Each side of the film thereby receives identical processing treatment.

On reaching the bottom of the developer rack, the film is caused to reverse its direction by an arrangement of rollers which has become known as a "turn-around." One form of this device is shown in Figure 7A and consists of a large, driven roller around which are positioned three smaller driven rollers and two guide shoes. The shoes and the small rollers, known as "cluster rollers," cause the film to turn 180° around the large or "master" roller, after which it continues vertically upward between the staggered rollers which form the opposite side of the rack.

On reaching the top of the rack, the film enters an arrangement of rollers and shoes very similar to that used in the "turn-around" just described, but inverted to cause the film to leave in a downward direction, and offset, with regard to the developer rack, to cause the film to pass on to the stop-bath rack. When so used, these rollers make up what is known as a "cross-over," as illustrated in Fig. 7B.

As shown in Fig. 6, the processing section has four stages: developer, stop bath, fixer, and wash. The processing racks and cross-overs used in each of these positions are substantially identical. In each case, the solution on the film surface is displaced by the action of the rollers in contact with the film and is replaced by relatively fresh solution from the larger volume in the tank. This action provides substantial agitation at the film surface, resulting in uniformity of development and permitting normal completion of the action of each of the solutions in a short time of treatment — in this case, 60 sec in each solution.

Control of temperature and uniformity of chemical composition throughout the system are attained by recirculating each of the processing solutions continuously through a system of heat exchangers in which the water used for tempering purposes is finally delivered to the wash tank. In the developer recirculation system, a thermostatically controlled electrical heater is provided to increase the flexibility of the system. In addition, the developer is filtered continuously by being recirculated through a replaceable, cartridge-type filter.

Replenisher solution is delivered to each of the processing systems by means of a pump which operates only while film is being fed into the machine. Thus, by controlling the rate of flow through the pump, the solutions are replenished at a rate that is directly proportional to the film load.

Film Dryer

After being transported through the wash rack, the film enters a special "exit cross-over," which causes it to turn only 90° instead of 180° and delivers it horizontally to the dryer. The "exit cross-over" is similar to the "entrance cross-over" mentioned earlier as accepting the film delivered by the rollers in the feed section.

On entering the dryer, the film first passes through a pair of driven, soft-rubber wringer rollers which effectively remove all remaining surface water. It then

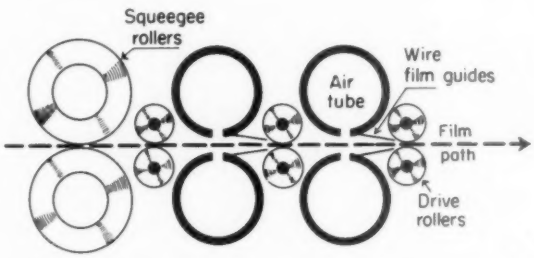

Fig. 8. Arrangement of rollers and air-distributor tubes used in dryer of X-Omat Model M Processor.

passes on to driven transport rollers, arranged in pairs as shown in Fig. 8. These are spaced 3 in. apart and carry the film through the remainder of the dryer.

Between each pair of transport rollers and located above and below the film plane are the air-distributor tubes having slit orifices through which high-velocity hot air is directed at both sides of the film. Because the leading edge of the film is unsupported between pairs of transport rollers, there is a tendency for it to vibrate vertically as it is subjected to the aerodynamic forces in the opposing jets. However, this tendency is controlled by the use of small guide wires anchored in the surface of the air-distributor tubes, which limit the amplitude of the vibrations and direct the leading edge of the film between the next pair of transport rollers. Since only the extreme leading edge of the film comes in contact with the wire guides, there is no tendency to abrade the film from this cause.

The relationships between transport rollers, air-distributor tubes, and guide pins used in the Kodak X-Omat Dryer are shown in Fig. 8.

As shown in Fig. 6, the remainder of the dryer consists of the motor and blower for recirculating the air in the dryer, a heater, filters, and the necessary ducting for delivering air to the distributor tubes. In addition, provisions are made for venting off a small proportion of the total air recirculated, and for bringing in an equivalent amount of filtered air.

In a normal film dryer, little attention need be given to the condition of the film surface from the time it is squeegeed to the time it is dry. However, in the roller transport system, consideration must be given to the fact that a changing and more or less tacky film surface comes in contact with transport rollers intermittently throughout the drying operation. It is for this reason that, in addition to the design characteristics of the dryer itself, special attention must be given to the nature of the photographic emulsion and to the chemistry by which it is to be processed in setting up any system of roller-transport processing.

In the X-Omat dryer, lightweight phenolic rollers having a textured surface to minimize the area of contact have been found satisfactory for use as transport rollers. Rotation of these rollers is maintained constant to avoid any hesitation which almost always leads to sticking. Care is used to assure uniform distribution of the drying air, since even minor variations in drying rate can cause drying patterns. High drying temperature is avoided in the dryer to minimize any tendency for the emulsion to soften during drying. With Blue Brand X-Ray Film, drying is accomplished in less than 60 sec at a dry-bulb temperature between 115°F and 125°F, depending on the quality of the drying air.

A normal question is, to what extent can roller-transport processing be applied to other sensitized products in their many forms? At this stage, only generalizations can be made.

Among the conditions most unfavorable to roller-transport processing are (a) the use of soft film emulsions, which have a tendency to stick to rollers, (b) the use of high processing temperatures which may have a softening effect, even on relatively hard emulsions, (c) the use of chemical formulae having an unusual softening effect on the film emulsion, (d) the use of a film product having a strong tendency to curl, and (e) the need for excessively high drying temperatures.

From this it is evident that only those films which can be processed to the required sensitometric level without undue softening of the emulsion or gelatin-back layers are potential candidates for roller-transport processing. Film having a strong tendency to curl, such as roll-camera film, can ordinarily be developed on roller-transport equipment by the use of a short length of a noncurling material attached to the leading edge of the film to prevent it from wrapping around the rollers. Limited experience has shown that continuous lengths of many films of any width an inch or two narrower than the length of the transport rollers can be successfully processed on suitably proportioned roller-transport equipment. Where space is sufficient, two or more strands can be processed, side by side in parallel, thus increasing the output of the equipment.

In view of the obvious advantages of a system of this type, investigation of the requirements for successful application of roller-transport processing to a wide variety of film products is continuing in the various divisions of the Eastman Kodak Company.

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Rapid Processing of X-Ray Film

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A method of transporting sheet-film materials has been made available in the Kodak X-Omat Processor which is described. It permits the application of rapid-processing techniques to these films. Kodak Royal Blue and Blue Brand X-Ray Films can be processed and dried in a total time of 6 min. This rate of processing is accomplished by (a) use of elevated temperatures in all the solutions, including the wash water, (b) use of active solutions, (c) optimum agitation by means of the wringer-roller transport system, and (d) drying with heated jets of air while the film is being transported between rollers.

Methods for the rapid processing of photographic films have been described by many workers[1,2,3] and pertain generally to the use of continuous lengths of specially manufactured narrow-width films, usually 16mm, 35mm, or 70mm.

A processing machine, Kodak X-Omat Processor, Model M, has now been specially designed for the handling of sheet-film materials and is discussed in the paper "A Self-Threading Processor and Dryer for Use with Specific Sheet Films," by C. J. Kunz and H. D. Russell.* A chemical cycle has been developed for the rapid processing of large sheets of Kodak Royal Blue and Blue Brand X-Ray Films.[4] The chemistry of the processing cycle and its relation to the film-transport path are discussed in the present paper.

Processing Chemistry

Kodal Royal Blue and Blue Brand X-Ray Films can be processed and dried in a total time of 6 min in the Kodak X-Omat Processor. This represents a reduction in processing time of about 1 hour compared to the hand processing systems which require 5-min development, 30-sec rinse, 10-min fixation, 15-min wash, 30-min drying and time for loading and unloading film hangers. The rate of processing on the X-Omat is accomplished by employing an active developer, a hardening stop bath, a rapid fixer, efficient washing, and processing at essentially 80°F under conditions that provide active surface agitation and film-squeegeeing between baths. The time of treatment in each processing solution is essentially 60 sec.

In general, the chemicals have been compounded as replenishers in such a manner that the replenishment rate of each is the same; that is, 1 gal of replenisher solution for each fifty 14- by 17-in. films processed. In the case of the developer, it is necessary to add a starting powder to the developer-replenisher solution. Extensive exhaustion tests of this procedure have shown that the photographic quality can be maintained for several thousand films.

Agitation

Rapid tank development of 14- by 17-in. sheets of double-coated x-ray films for times of development of 1 min or less usually results in a poor-quality radiograph because the development is not uniform. This result is caused by uneven streaming of the reaction products of development over the surfaces of the film. The reaction products retard development and prevent the relatively fresh developer from contacting the emulsion surface. In order to obtain a uniformly processed sheet, the reaction products must be removed as rapidly as they form by an efficient surface agitation system which is provided by the wringer-roller system in the X-Omat Processor.

Temperature

The maximum temperature that can be tolerated in a processing system is determined primarily by the nature of the photographic emulsion being processed, especially with respect to hardness, gel thickness, swelling characteristics, and, to some extent, the chemical processing cycle. However, temperatures above 100°F usually produce excessive swelling unless the emulsion is specially hardened in manufacture.

Development

The Kodak Rapid X-Ray Developer was found to be the most satisfactory formula for the rapid processing of Blue Brand X-Ray Film. The developer-replenisher formula for the X-Omat Processor is an improved liquid version of the Kodak Rapid X-Ray Developer Replenisher powder which, when diluted with the starter solution recommended, provides development activity equal to that of Kodak Rapid X-Ray De-

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*See page 27, this journal.

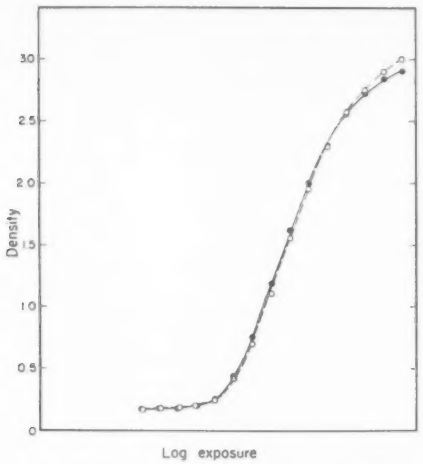

Fig. 1. Sensitometric characteristics of Kodak Blue Brand X-Ray Film. O— —O processed on X-Omat; ●——● tank 4 min at 68 F.

veloper. The salt content of this solution is sufficiently high to prevent excessive swelling at elevated temperatures.

The sensitometric characteristics of a radiograph processed on the X-Omat Processor were essentially the same as those obtained by tank development in Kodak Rapid X-Ray Developer in 4 min at 68°F. These data are summarized in the table and illustrated in Fig. 1.

	Time (min)	Temperature (°F)	Contrast	Relative speed	Fog
Tank	4	68	2.55	100	0.06
X-Omat	1	82	2.55	97	.06

Hardening Stop, Fixation, and Washing

The choice of the proper processing cycle is determined by the degree of hardening necessary to prevent excessive swelling of the emulsion, to toughen the surface so that it will not be readily scratched, and to prevent excessive tackiness during drying. Most films dried in the normal manner go through a critical drying period in which the films become very tacky, just before they are dry. In the X-Omat Processor, the water is removed very rapidly from the film and this critical drying period is of short duration. The tackiness during drying depends upon (1) the pH and composition of the stop and fixing baths, (2) the degree of swelling of the emulsion, and (3) the hydrophobic or hydrophilic nature of the emulsion surface after drying.

In compounding an efficient processing cycle, it is desirable that the number of different solutions and the time in each solution be at a minimum. In normal practice, the hardener is usually incorporated in the fixing bath, but it is possible to use a hardening stop bath and provide more latitude in compounding the fixing bath so that hypo can be removed readily during washing.[5]

The hardener stop bath and fixer combination is a chemical system which has been compounded to harden the film surface in such a manner that it will show the least tackiness during drying and also permit rapid washing of Royal Blue and Blue Brand Films. The hardener stop-bath formula is a liquid version of the Kodak Hardener F-5a* without sodium sulfite. The useful pH range of the stop bath in practice is slightly below the isoelectric point of the gelatin. When the pH value is above the isoelectric point, swelling occurs and the tackiness is excessive.

The fixing bath is a relatively high pH formula similar to Kodak Fixing Bath F-24** compounded with ammonium thiosulfate for rapid fixing and rapid removal of hypo during washing.

The effect of the pH value of the fixing bath on the removal of the hypo during washing is shown in Fig. 2. Curve A shows that, for a given hardener

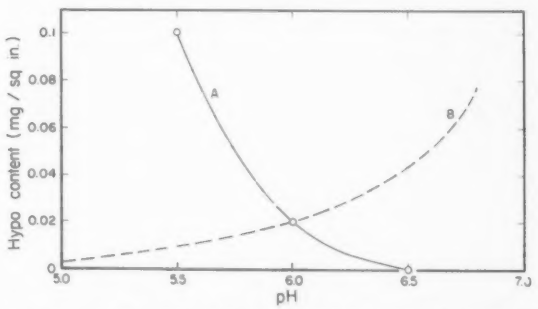

Fig. 2. Effect of fixing-bath pH on hypo elimination and film tackiness Curve A shows residual hypo at different fixing-bath pH values after 60-sec washing, e.g., 0.10 mg/sq in. hypo at pH 5.5; zero at pH > 6.5. Curve B shows relationship between fixing-bath pH and emulsion tackiness.

formula, the pH value of the fixer determines to a large degree the completeness of the removal of the hypo in the given time of 60 sec. The hypo content of the film at a pH value of 5.5 is equivalent to 0.1 mg/sq in.; at a pH of 6.0, it is 0.02; and, above a pH of 6.5, it is zero.

Blue Brand X-Ray Film with a hypo content of less than 0.04 mg/sq in. is considered to be washed satisfactorily for archival keeping.

Curve B in Fig. 2 is hypothetical but indicates the relationship between the tackiness of the film during drying and the pH of the fixer. Although a high-pH fixing bath is desirable for more rapid washing, it also

*Kodak Hardener F-5a has the following composition: Water, about 50°C, 600 cc; Kodak Sodium Sulfite, desiccated, 75 grams; Kodak Acetic Acid, 28%, 235 cc; Kodak Boric Acid, crystals, 37.5 grams; Kodak Potassium Alum, 75 grams; water to make 1 liter.

**Kodak Fixing Bath F-24 has the following composition: Water, about 50°C, 500 cc; Kodak Sodium Thiosulfate (Hypo), 240 grams; Kodak Sodium Sulfite, desiccated, 10 grams; Kodak Sodium Bisulfite, 25 grams; water to make 1 liter.

tends to produce a film with a greater degree of tackiness during drying. Since the film is being transported during drying between rollers, this tackiness has to be kept to a minimum or satisfactory transport of the film is not possible.

The X-Omat Processor provides excellent agitation and an effective squeegeeing action, making it possible to use processing solutions that cannot be used satisfactorily in other processing systems. The hardening stop bath and fixer combination produces minimum swelling, minimum tackiness, and maximum washing. The combination of machine design and chemical formulation have reduced the volume or weight of solution retained by the film and carried into the next solution.

The average carry-over of developer for a 14- by 17-in. x-ray film in tank development is between 60 and 90 grams. Much smaller quantities are carried over in the present processing system. For example, carry-over from the developer is approximately 8 to 9 grams; from the stop bath, 12 to 13 grams; from the fixer, 11 to 12 grams; and, from the wash water, 10 to 12 grams. These quantities represent measurements made in fresh solutions and also throughout the exhaustion life of the solutions.

The quantity of solution carried out of each bath by the film also indicates the degree of swelling of the emulsion in that solution. In this cycle, the small quantity of water remaining in the film after washing not only aids in rapid drying but also greatly reduces the tackiness of the films during drying. When the water content is greater than 15 grams per 14- by 17-in. x-ray film, the film dries poorly and has a tendency to be very tacky.

Drying

The wringer-roller dryer is very efficient for sheets of Royal Blue and Blue Brand X-Ray Film up to 14- by 17-in. in size. Both sides of the film must be dried simultaneously within a few seconds to avoid drying streaks. Otherwise, successful drying is intimately related to the processing cycle and the tackiness of the emulsion.

The hydrophobic or hydrophilic nature of the dried emulsion surface can be used as an indication of the most effective processing cycle with respect to tackiness. A simple test to determine this surface property involves the application of printers' ink (oil base) to the moistened surface. The dry film which will take ink which cannot be rubbed off is considered to be hydrophobic and that film from which ink can readily be removed is hydrophilic.

In general, it can be said that the hydrophobic–hydrophilic nature of the emulsion follows the hypothetical tackiness curve, B, in Fig. 2. Films processed with a fixing bath of pH less than 6.0 tend to be more hydrophobic; and, as the pH of the fixing bath increases above pH 6.0, the emulsion tends to be more hydrophilic.

Therefore, the processing cycle for Royal Blue and Blue Brand X-Ray Films produces a strong hydrophobic surface and consequently less tackiness during drying.

A system has been described that involves the design of the machine for processing Kodak Royal Blue and Blue Brand X-Ray Films, and a processing cycle. The application of the processing principle to other films will require further research.

Acknowledgment

The many suggestions and ideas of my associates are very much appreciated, particularly the contributions to the basic processing cycle made by M. D. Little and C. F. Amering.

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A Telescope System for Missile and Satellite Photography

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A long focal length telescope has been designed for missile photography at slant ranges greater than 100 miles. The performance of the telescope and the effect of the environmental factors are discussed. A diffraction test for precise field focusing is described.

The last decade has seen the increasing use of reflecting telescopes for aircraft, missile, and satellite photography. The Recording Optical Tracking Instrument Mark II has been developed for the Atlantic Missile Range by The Perkin-Elmer Corporation as an integrated system which attempts to control those instrumental and environmental factors which decrease information available in the final recorded image. It represents an effort not only to produce an optical system capable of high laboratory resolving power, but also to maintain this performance during actual field missile photography by the integrated design of the telescope, the tracking mount, the telescope buildings, and all auxiliary equipment required to minimize the lowering of resolution and contrast by the dynamic factors of focus, exposure, image motion and vibration, and the environmental factors of temperature and atmosphere.

The Telescope

Because of the uncertainty of the atmospheric characteristics and to retain flexibility for the various missile programs, the telescope was designed with five effective focal lengths, 100, 200, 300, 400, and 500 in. A 24-in. aperture was selected because of the general opinion at that time that it was the largest practical diameter possible. The actual optical design was strongly influenced by the requirement for quick change of focal length and the necessity to minimize the nonimage-forming light which could reach the film plane. Since earlier systems sometimes contributed up to one-half stop of contrast-lowering light, this is an important consideration for long-range photography where the contrast eventually approaches zero.

The telescope (Fig. 1) is of a Newtonian form with the 24-in. Pyrex parabola having a focal length of 100 in. The prime image plane is at the reticle. The series of five amplifying systems correct primarily for coma and astigmatism while magnifying the prime image by factors of 1, 2, 3, 4, and 5. Each of the amplifying systems contains aperture stops which, with the diaphragms in the main telescope tube, greatly reduce the nonimage-forming light which might reach the film plane. The final flat image plane covers a $2^1/_4 \times 2^1/_4$-in. aperture of a 70mm camera. The laboratory resolution by Air Force test standards varies from $^1/_2$ sec of arc at 100-in. focal length, to $^1/_3$ sec of arc at 500-in. focal length. Resolution at the edge of the field in all cases exceeded the specified one-half of axial performance. The collimator used was a 24-in. $f/10$ parabola with the telescope rotated to determine the off-axis resolution.

To preserve this performance in the field, the telescope tube was required not only to be rigid enough to prevent 0.001-in. deflection during the missile tracking and to minimize the effect on the optical elements of the high-speed camera vibrations, but also to shield the optical elements from the effect of changes of environment. This was accomplished by making the rear section, which carries the camera, a heavily ribbed aluminum casting, while the forward section is a lightweight bonded sheet aluminum structure.

This hollow forward section acts to minimize the effect of solar heating since, being close to the dome opening, it is most apt to be struck by sunshine.

To further minimize the heat transfer which creates thermal air gradients and convection currents within the tube, the open end is closed by a plane-parallel optical-glass window and the entire length of the tube interior is lined with $1^1/_4$ in. of insulation. These measures play an equally important role in minimizing the thermal changes of the optical elements. Temperature variations are damped sufficiently to permit the use of temperature compensation corrections based on scale changes rather than sharp dynamic effects of an uninsulated or open system.

Tracking Mount

Having assembled a 3,000-lb telescope capable of high resolution, the next step was to track with it to the same degree of precision. This was attempted

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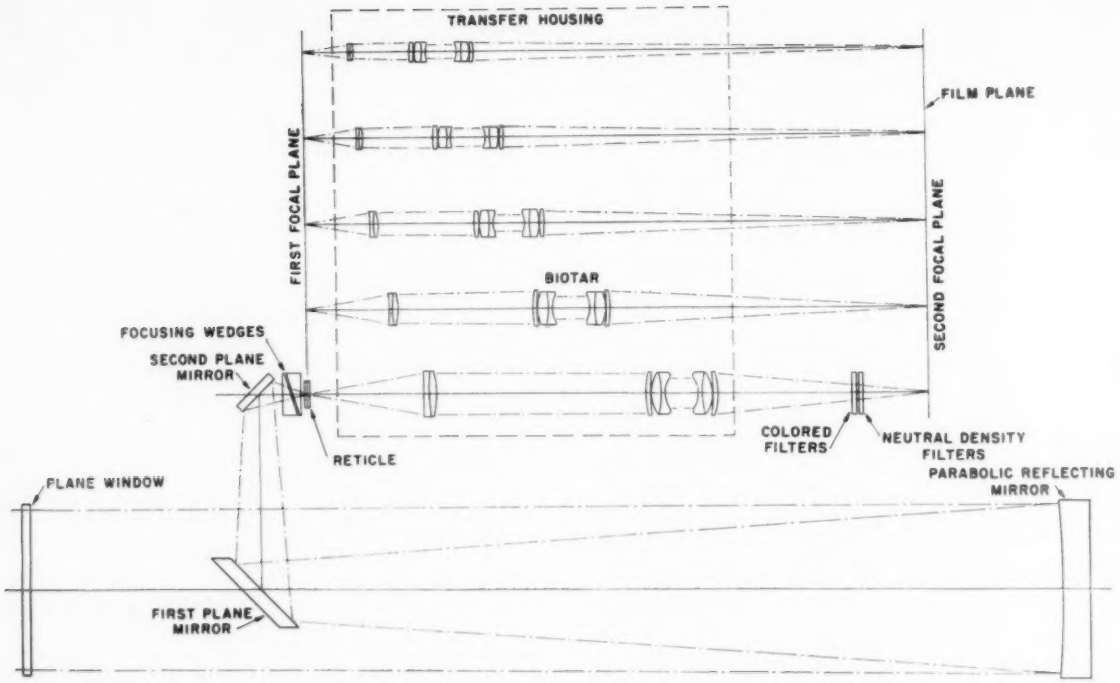

Fig. 1. Schematic of ROTI Mark II Telescope optical system. The focusing wedges are used to maintain prime focus at the reticle. This allows any one of the five amplifying reimaging systems to be rotated into position and used without refocusing. The light paths shown within the transfer housing are not precise. The doublet is a $-2\times$ magnifier which decreases the initial divergence and allows the Biotar to accept the full bundle from the prime image.

with an electrohydraulic drive on a greatly modified 5-in. Mark 31 Naval gun mount. The problem here is very similar to the image-motion compensation problem in aerial photography. The telescope must follow the missile with a precision which will prevent loss of resolution and contrast because of relative image motion. For 500-in. focal length, $2^1/_4$-in. format, and 10-msec exposures, this means that the tracking error cannot exceed 7 min of arc if the missile is to be in the frame, while the tracking error cannot change by more than 10 sec of arc per sec if resolution is to be maintained. Vibrations of this magnitude must also be prevented from reaching the telescope optics.

After a critical study of the 5-in. gun mount, the 84-in. azimuth bearing and gearing assembly, with an axial wobble adjustable to less than 10 sec, was the only assembly retained without extensive modification. The hydraulic pumps, powerful vibration sources, were removed from the mount and housed in a separate structure. The electrohydraulic servo control system was redesigned to achieve precise tracking for both smooth flights and the erratic flights which interest the missile engineers.

In the aided-tracking mode of tracking, the operator observes the missile through a 10-, 20-, or 40-power sighting telescope and applies a fingertip force to the knob of a "stiff-stick" control when he sees that a tracking error exists. This force deflects the rigidly clamped stiff-rod on which is mounted a pair of bridge capacitors. The small deflections unbalance the bridge circuits. The resultant voltages determine the position, velocity, and acceleration required for the aided-tracking control of the hydraulic system.

The "stiff-stick" control offers both vector control of movement and an almost infinitely sensitive control of rates not limited by the limitations of human limbs. The proportionality constants for position, velocity, and acceleration can be adjusted for operator and missile to approach the goal of one control motion resulting in the correct position and velocity after the error is seen in the eyepiece of the sighting telescope.

If the operator cannot see the target, he can either use the visual null system which visually presents a radar determined vector to the target, or he can switch the mode of control to "remote," which allows the mount to follow radar directions to the target.

The use of remote and aided control systems has maximized the precision of tracking by the operator and the mount. Tracking errors rarely exceed 2 min of arc with smooth trajectories showing errors of 30 sec rms. The stability of tracking results in only a minimum percentage of pictures taken with the telescope-missile relative angular velocity exceeding

10 sec of arc per sec. The maximum tracking rates are 10 deg/sec of velocity and greater than 6 deg/sec of acceleration. For acquisition of the target a slew rate of 20 deg/sec is available.

Environmental Factors

The first of the measures taken to minimize the environmental effect on performance — the tube design — has already been described. The closed insulated telescope tube is intended to insure that the air within the telescope tube be homogeneous and that the thermal deformation of optical elements be minimized. These heat transfer effects are particularly important for missile work, since operations are normally on sunny days.

Two added measures are taken to assist in minimizing the thermal effects. An astronomical dome is used as an instrument shelter. It ensures that the instrument remains shaded during the greater portion of the mission. Air conditioning of the dome interior ensures that the instrument has been brought to ambient air temperature and is at equilibrium with the outside air before the dome is opened.

The effect of the environment on performance characteristics which is hardest to control is that of the atmosphere. The atmospheric variations in index of refraction which degrade resolution are those located close to the surface of the earth and in layers at 30,000 to 40,000 ft or more. The ground layer can be controlled to some extent by the choice of location for the instrument. The obvious first step is to place the telescope as far above the ground as is economically feasible. The second step is to attempt to place the telescope line of sight over terrain which contains a minimum of temperature variations, since this minimizes local convection currents or bubbles and variations in the index of refraction in the line of sight.

Because of these considerations the telescopes were placed on reinforced concrete towers (Fig. 2) as close to the ocean as the terrain allowed. The line of sight is 25 ft above ground level and above the layer of salt spray from the ocean. It is essentially an overwater sight through frequently almost homogeneous air.

The wisdom of the selection is borne out by lunar photographs taken at this site which are comparable to those from astronomical mountain-top telescopes of equal aperture.

This discussion illustrates the complexity of the environmental factors. The effectiveness of the measures to minimize the effect of the environment on the instrument and the location of the instrument can vary the results significantly, particularly in considering performance of larger aperture telescopes.

Operating Conditions

The photographic products of tracking telescope operation fall roughly in two categories. The first might be called the autopsy data. For slant ranges roughly under 65 miles one can see structural missile details. Engineers are interested in correlating missile behavior with possible abnormal structural or flame changes visible in the frame. They are usually trying to determine if a given detail was still in place at the time of malfunction. Theirs is primarily a detecting rather than a resolving problem.

As the missile travels to greater slant ranges from the station, the problem becomes one of determining the attitude and length of what appears as a line target. At still greater ranges, interest is focused on detecting separation of missile stages.

In both cases the most important consideration is the maximizing of contrast rather than the resolving of high contrast objects, as is the case in stellar observations at night. The effect of the atmosphere is also slightly different in stellar observations. For astronomical targets we have essentially a static target with the atmospheric discontinuities slowly moving across the line of sight. In the case of the missile, the target is traveling across a hundred or more atmospheric cells or discontinuities. The result is a lowered contrast between missile and sky which is less aperture-dependent than in the case of the semi-stationary objects in astronomy.

To maximize the contrast, two features, auto-focus and auto-exposure, have been incorporated in the tracking telescope. The need for dynamic automatic focusing is highly emphasized by the 400-mile hyperfocal distance for the 500-mile focal length. This hyperfocal distance is based on one-fourth the Rayleigh limit as the criterion for focusing for low-contrast cases.

The depth of field varies from 160 ft at a slant range of 20,000 ft, to 4,000 ft at 100,000 ft. This is 0.008 in. at the film plane and 0.0003 in. at prime focus.

If the contrast in the object is to be retained in image plane, the telescope must be focused with this

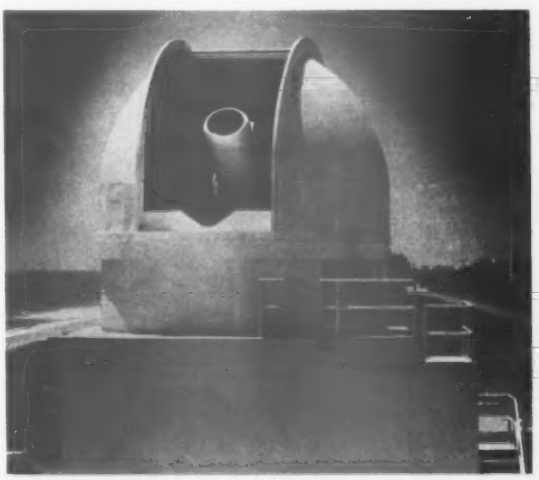

Fig. 2. ROTI Mark II Tower. The telescope and dome are shown in operating position at Melbourne, Florida.

preciseness. Since the thermal expansion of the system at the rate of 0.001-in./deg F can quickly exceed these tolerances, any automatic focusing system must also include a temperature compensation system. The telescope tube design philosophy which attempts to isolate the tube interior from the environment performs a second service in increasing the thermal time constant of the telescope system. This allows a measurement of the differential expansion between the aluminum tube and an invar rod to be used to compensate for temperature changes. The correction for temperature and slant range are both introduced in the auto-focus unit which performs the focusing by moving two $15^1/_4$-deg prisms located immediately before the prime reticle. Optically the two prisms are the equivalent of a plane-parallel plate of glass of variable thickness. The lateral movement of the prisms changes the equivalent optical thickness of the pair which moves the image along the optical axis to the prime reticle. The movement of the prisms is linked by a precision gear train to a potentiometer. The voltage at the moving contact indicates the prism positions. A simple bridge compares this voltage with the radar-supplied slant range voltage and then controls a servo motor which moves the prisms to the optical thickness required to position the image at the reticle and film planes.

To introduce the temperature correction, a mechanical differential between the potentiometer and the prisms is used to change the relationship between the two. The differential serves to make a new prism pair thickness correspond to a given potentiometer voltage value. It acts as a bias on the slant range focus curve. Consequently, a given voltage corresponds to fixed slant range, while the actual effective glass thickness at any given slant range of the prism pair varies with the thermal expansions.

During the operation of the telescope, exposure is controlled by the auto-exposure unit in order to achieve maximum missile sky contrast. As the range of the missile approaches the region where image contrast approaches zero, even detection requires that the illumination at the film plane be kept at a level which will ensure maximum density difference. Light from the region surrounding the 70mm frame is compared with a standard source. Two opposed variable transmission Inconel discs mounted before the film plane are rotated to vary the illumination until it balances that of the standard light source. Since the light sampled by the auto-exposure unit is from the background sky around the missile, it is only the background sky density which is maintained at a density of 0.6 for a maximum density difference between the missile and the sky. This condition is ideal when the missile appears as a point at the image plane. It is not ideal when the missile is a resolvable area smaller than the 70mm film frame. In this case the missile image is overexposed where the reflections are specular and underexposed for the shaded portion. It is interesting to note that, since the missile quickly climbs above the cloud layer, the illumination on it is relatively constant and not dependent on the brightness of the background sky.

Diffraction Focusing

The optical system used on ROTI Mark II has five focal lengths, 100- to 500-in., which must have the same final image plane. The focal lengths are determined by the five amplifying systems which have only one common conjugate distance. The re-establishment of this distance when cameras were changed presented a problem in the field. The practical realization of the performance level established for the instrument hinged on the ability to focus the telescope for all five focal lengths.

A simple diffraction test was devised which allowed the film plane to be determined by one man in less than two hours.

A partially obscuring pattern is placed over the aperture of the telescope in order to produce a coarse diffraction pattern which can be readily observed at the film plane. The pattern consists of two 5 × 8-in. sets of three 1 × 8-in. parallel rectangular openings separated by two 1 × 8-in. obscuring bars. Both sets of three slits are at the extreme ends of a common diameter which is perpendicular to and bisects all the slits. Each set of three slits produces a diffraction pattern with the second maxima approximately $^1/_{13}$ mm from the central maximum. When the system is focused, the film and image plane coin-

Fig. 3. Diffraction test example. The focus setting is changed as the stellar images move across the field. The double maxima at the ends of the trace are the result of poor focus. The maxima become superposed at best focus indicated by the arrow.

cident, the film records only one diffraction pattern with one central maximum and two weaker secondary maxima. When the system is not in focus, the pencils of converging rays from each of the two sets of slits form two diffraction patterns at the film plane. Each pattern has its central maximum and two secondary maxima. As proper focus is approached, the two diffraction patterns act as verniers as they become superposed, first to two central maxima with three secondary maxima, then to one broad central maximum with indistinct minima and secondary maxima. The correct focal plane results in one sharp central maximum with two distinct minima and secondary maxima.

In actual use second-magnitude stars approximately 15 deg from the celestial pole are used as sources. With the slits tangent to the apparent circumpolar motion of the star, the star is allowed to drift across the telescope field, while the settings for the focusing prisms are varied (Fig. 3). The resultant images of the moving stars are lines on the emulsion. The use of at least two or three seconds of exposure time per focal setting allows the averaging of atmospheric effects.

The geometry of the system had led us to expect the ability to detect a 0.001-in. focus error at the prime plane. In actual practice, with reasonable atmospheric turbulence conditions, it is possible to detect an error of 0.0003 in.

Conclusion

ROTI Mark II photographs with resolution of approximately 1 sec of arc at slant ranges under 13 miles (Fig. 4) which indicates that the adaption to the immediate environment has been successful. It also verifies past observations that a line of sight over a body of water ensures minimum variations in the refraction of air because of the minimum variation in the temperature of air over water.

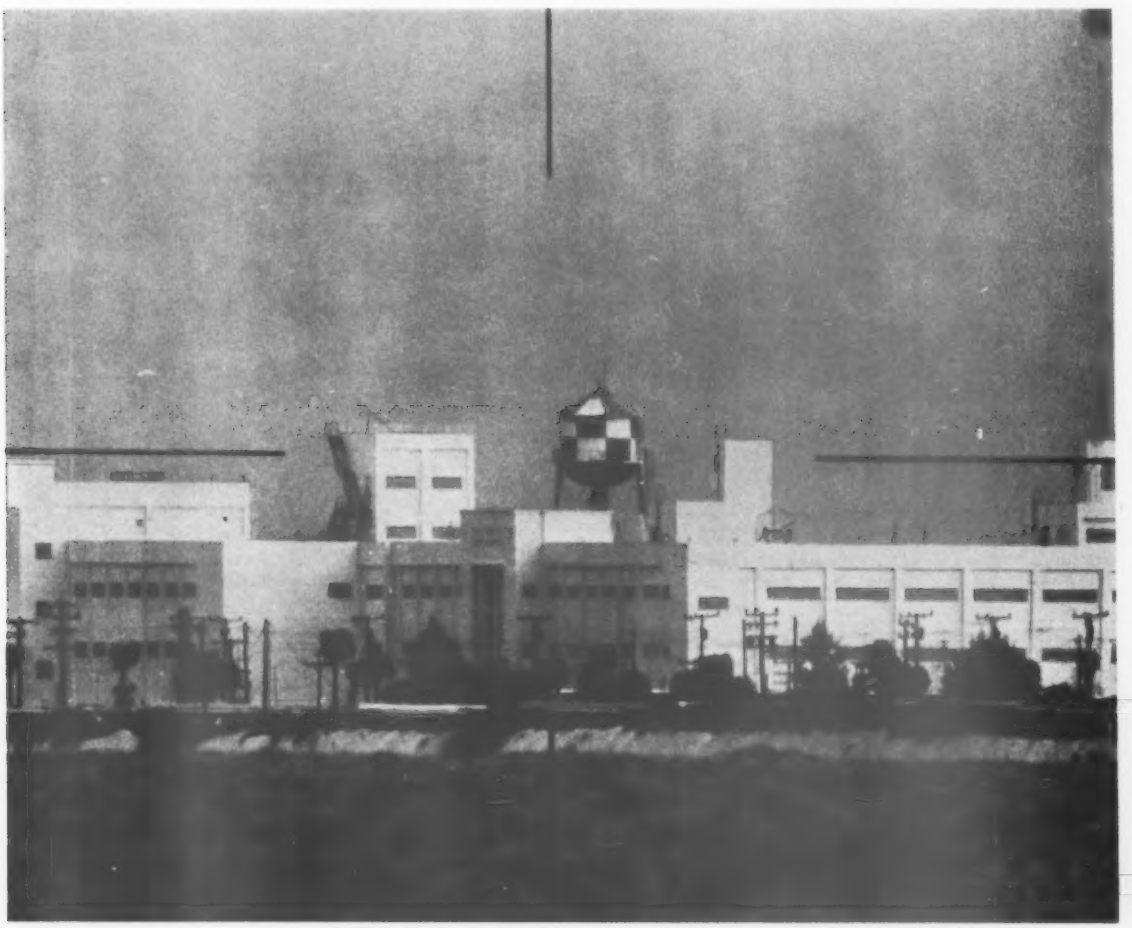

Fig. 4. A 500-in. focal length photograph of building 13 miles from telescope. Resolution of 1 sec of arc is found in the original negative.

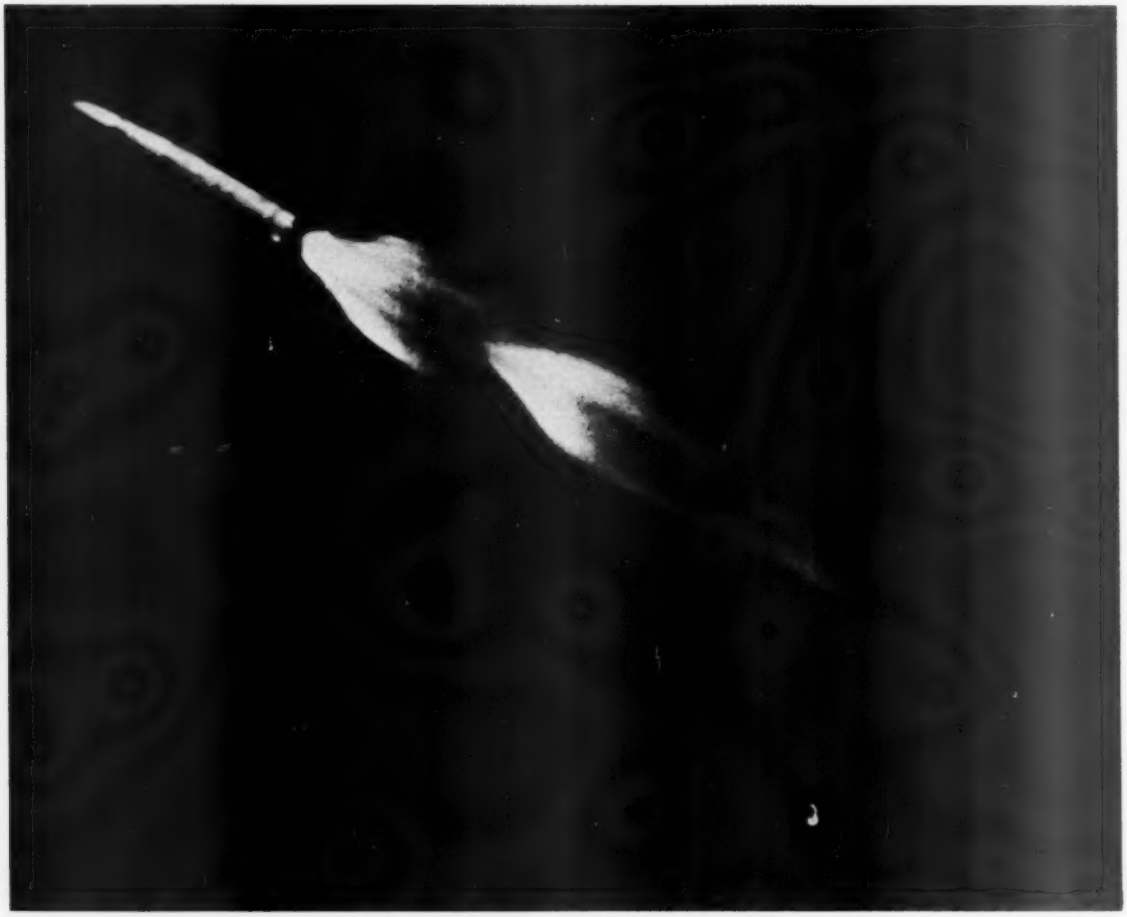

Fig. 5. Thor missile at 35 miles with 500-in. focal length.

In actual missile use this allows high resolution during the early missile flight, photographing details which subtend less then $^1/_3$ sec of arc (Fig. 5). During the final stages of flight the missile becomes a line without significant detail. The problem here becomes one of detection rather than resolution; contrast between missile and background is sought.

The greatest improvement in this area stems from the proper choice of launch time to increase the target-to-sky contrast. This has made it possible to photograph missiles at distances of 200 miles in the daytime, while twilight operation ensures photographs at distances of 400 miles with significant information recorded.

To perform effectively for missile photography, a large aperture telescope must be designed with high resolving power. The dynamic factors of image motion, vibration, focus, and temperature must be controlled. These measures must be supplemented by the optimum adapting of instrument to environment in order to realize maximum performance. Since successful missile photography primarily involves low-contrast targets, the minimizing of nonimage-forming light, the use of precise exposures, and the choice of firing times for maximum object contrast become necessary.

It is only by the maximizing of the characteristics of the instrumental, operational, and environmental factors that the meager object contrast can be transferred into a useful image contrast and resolution.

Acknowledgment

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• Book and Literature Reviews

Wörterbuch der Photo-, Film-, und Kinotechnik mit Randgebieten (Dictionary of Photography and Motion Picture Engineering and Related Topics)

Vol. 1. English — German — French. Wolfgang Grau. Verlag Radio-Foto-Kinotechnik GmbH, Berlin — Borsigwalde, 1958. 664 pp. (8 in. by $5^3/_4$ in.)

This is the first of a three-volume trilingual dictionary. Its pages are made up of three columns each, the first column listing English (and American) words and combinations in alphabetical order, while the second and third give the equivalent in German and French. About 16,000 terms in each language are included. The coverage of terms used in the technical photographic literature is very satisfactory for the most part, and is more extensive than that given in any other dictionary known to the reviewer. An occasional omission was noted, e.g. the diffusion-transfer process is not listed, and occasionally some space is wasted by entries such as "bromic silver" and "shrunking." The inclusion of chemical formulas of many of the compounds listed will aid some users of the dictionary, but a little more attention could have been paid to consistency in writing the formulas. These are minor blemishes, however, in a work which shows evidence of a large amount of labor well done. Volumes 2 and 3, when they appear, will be more useful to the English-speaking scientists and engineers, since they will list the German and French words, respectively, in alphabetical order. — *T.H.J.*

Mitteilungen aus den Forschungslaboratorien der Agfa Leverkusen-München (Communications from the Research Laboratories of Agfa Leverkusen-Munich)

Vol. II. H. Frieser, ed. Springer-Verlag, Berlin, Göttingen, Heidelberg, 1958. 338 pp., 263 illus.

The second volume of this series, edited by Prof. Dr. H. Frieser, has followed the first in a surprisingly short time and almost surpasses its predecessor in richness of content. In six articles, two newly added fields have been given special consideration: the parallels in our knowledge of the physics of semiconductors and of the primary processes of photography (R. Matejec and E. Klein), and the applications of communication and information theory to photography (H. Frieser and E. Zeitler). Reading these six communications, parts of which have not been published before, will afford an insight into areas which, in some instances, are at the frontiers of our knowledge. Of the remaining 18 works, nearly every one represents an investigation into an interesting specialized field of photography. Thus we learn about the number of exposure nuclei in the latent photographic image from investigations with the electron microscope, about the dependence on grain size of the absorption of quanta in photographic layers, about the properties of emulsion layers for exposure to electrons, and about new knowledge of the development process (E. Klein; H. Frieser). Among other works in the theoretical field are: "Effect of the Coating Thickness upon the Photographic Characteristics of an Emulsion" (E. Zeitler), "Reaction Mechanism and the Kinetics of Dye Coupling" (J. Eggers), "Chain-substituted Cyanine Dyes" (H. v. Rintelen), and "Silver Salt Formation by Photographic Stabilizers" (E. Klein).

Practical questions have not been neglected, as can be seen from the following subjects: "Regeneration of Photographic Developers" (H. Sassmann), "4-Amino-5-pyrazolone as Black-and-White Developer" (L. Burgardt and W. Pelz), "Change of Paper Contrast upon Additional Exposure"' (H. Berghaus), "Modification of Contrast of Commerical-Type Photographic Material by Combining Short and Long Exposure Times" (J. Eggers), "Spectral Sensitivity of Some Agfa Films" (R. Müller), "Graphic Determination of Optimum Colors" (E. Hellmig), "Investigation of Color Memory Capacity" (E. Hellmig), and "Control of Light in Photographic Copying Apparatus Equipped with Exposure Regulator" (F. Biedermann and R. Wick).

With great devotion and much industry, a dozen young researchers have carried out the ingenious experiments on the aforementioned subjects. They may be assured that their work will offer the scientific photographic world some stimulating suggestions. Prepared by the publishing house of Springer with traditional care, this book is warmly recommended to the respective technical circles. No special insight is required to predict a great success for this beautiful work.

The Journal of the Society of Scientific Photography of Japan

Vol. 21, No. 2, June 1958

"Characteristics of Photographic Materials Sensitive to Electrons," Mataichi Tajima, pp. 58-63, 64-70. An increase in photographic speed for light photography can be obtained under some conditions by making a uniform exposure to light before (hypersensitization) or after (latensification) the image exposure. These are well-known procedures. In the first of two papers (actually parts III and IV of a series) published under the above title, Mataichi Tajima considers the possible extension of such double-exposure

methods to the photographic recording of electron beam images. The effects of various combinations of double exposure to light, x-rays, and electrons on the speed of Fuji photographic materials used in electron microscopy were tested. The uniform exposures were adjusted to produce a fog density of 0.05 or 0.15 when used alone. For electron image formation, an increase in speed of 1.5 – 1.8 was obtained by giving the material a uniform exposure to 50 or 100 kev electrons for 5 min prior to the image-forming exposure, and an increase of about 1.4 fold was obtained by giving the uniform exposure after the image exposure. An increase in speed for electron recording also was obtained when the material was given a uniform exposure to 100 kv x-rays after the image exposure, but uniform pre- or post-exposure to light generally was not useful.

Little or no hypersensitization for light image or x-ray image formation was obtained by pre-exposure to light for 0.1 sec. A 5-sec post-exposure to light produced a marked latensification of a light image formed by high-intensity exposure, had a smaller effect on an image formed by low-intensity light, and only a slight effect on an image formed by x-rays (80 kv).

Possible effects of unintentional secondary exposures during the use of the electron microscope, arising from fluorescent light emitted by the emulsion layer or secondary radiation emitted by the glass plates during electron bombardment, were tested experimentally with Fuji Process plates. The results indicate that no significant effects of this kind occur.

In the second paper, various factors which influence the contrast of the negative are discussed, and data are given on the relation of contrast to time of development for several developers. To obtain good electronmicrographs for interpretative purposes, the author recommends that the product of the gradations of the negative and positive materials, $\bar{G}_n \cdot \bar{G}_p$, should be at least 1.5. Suitable developers for electronmicrographs of specimens of high, normal, and low contrast are discussed and some experimental formulas suggested. To obtain high negative sensitivity and contrast, the double exposure technique already described was used, together with a special developer of the composition: D-72, 500 cc; hydrazine sulfate, 3 grams; 6-nitrobenzimidazole, 5 mg; and water to make, 1000 cc.

Images formed by electrons are prone to show the Kostinsky effect. The following precautions are suggested as a means of avoiding the effect: avoid excess exposure, use a developer which does not contain too much silver halide solvent and which does not have too high a pH, and agitate the developer well during development.

"Couplers and the Mechanism of Dye Formation in Color Development," Hisatake Ono, pp. 49–57. A review is given of the relation between the chemical structure and the absorption spectra of cyan, magenta, and yellow dyes used in color photography, and of recent advances in the mechanism of color development.

"Study of the Characteristics of Exposure Meters," Kiyoshi Okada, Yoshinobu Nayatani, and Isamu Ueda, pp. 71–9. The Japanese Industrial Standards for exposure meters, JIS B7120, were established in 1957. This paper describes the method of testing, discusses the physical meaning of the specifications, and gives results for 13 exposure meters of various makes. It includes 15 figures and 3 tables.

"Photomicrographic Observation by Motion Pictures of the Development of the Sub-macro Crystals of Silver Halides," Shin Fujisawa, Eiichi Mizuki, and Kikuo Kubotera, pp. 80–5. This paper describes and illustrates with 34 photomicrographs the results obtained in a motion picture photomicrographic study of the development of silver iodobromide crystals which had been grown to 70–80 μ diameter by slow evaporation of a saturated ammonia solution of silver halide. Much of the information given and many of the photomicrographs were reproduced earlier in *Science et industries photographiques*, *28:* 82–3 (1957).

All of the papers are in Japanese, but the captions to the figures and tables, and the summaries are in English.—*T.H.J.*

Non-Gelatin Photographic Emulsions

A series of four papers by F. Evva, of FORTE Fotokémiai Ipar, Vác, Hungary, describes his investigations on the preparation and properties of silver halide emulsions with synthetic colloids in place of gelatin. In the first paper, he groups the colloids into three classes on the basis of their effect on grain growth during the physical ripening stage of emulsion preparation. These classes are: (1) Colloids which surround the grain with an "elastic sheath," permitting growth in the presence of either excess silver or halide ions. Poly(methacrylamide), poly(vinylpyrrolidinone), and gelatin belong to this group. (2) Colloids which form a "rigid sheath," strongly restraining grain growth. This type includes poly(vinyl alcohol). (3). Colloids which form a "semirigid sheath," allowing grain growth in the presence of excess halide ion but not excess silver ion. This type includes polymeric carboxylic acids and certain acid-alcohol copolymers.

Evva's second paper describes the preparation and sensitization of silver bromide and silver chloride emulsions with poly(vinylpyrrolidinone) as the protective colloid. Emulsions were obtained which had speeds comparable to those of commerical contact papers.

The third paper deals with ammonia-type silver iodobromide emulsions prepared with poly(vinyl alcohol). These could be gold-sensitized by the aurous thiocyanate complex in the presence of a sulfur sensitizer such as allylthiourea or sodium thiosulfate. Spermin and polyethylenimine, added at the after-ripening stage, increased sensitivity; ethylenediamine added alone at this point decreased speed, but the ethylenediamine had a synergetic effect on sensitization by Spermin.

The gold-sensitized ammonia-type emulsions prepared with poly(vinyl alcohol) had a sensitivity equal to that of commercial enlarging papers, but the keeping properties were poor in the absence of a

stabilizer. Accordingly, tests were made on various stabilizers, and these are described in the fourth paper. Optimum results were obtained with benzotriazole. The effect of rhodium chloride, present during precipitation, on the properties of the silver halide–poly(vinyl alcohol) emulsions also was studied. Elfriede Brauer had found that rhodium chloride increased the photographic sensitivity of thallous bromide–gelatin emulsions, but the amount of rhodium chloride which produced optimum sensitivity in the thallous bromide emulsions desensitized silver bromide–gelatin emulsions. Evva found that rhodium chloride present during precipitation increased the dispersity of his ammonia-type silver iodobromide emulsion, but not of the neutral-type silver chloride emulsion. The rhodium chloride decreased the sensitivity of the iodobromide emulsion, but it caused a marked increase in contrast when the emulsion was gold-sensitized. (It caused only a small increase in contrast of the non-gold-sensitized emulsion.) Evva concludes that the effect of the rhodium chloride on the silver iodobromide emulsion is not due primarily to the change in grain size but rather to a topochemical effect on the sensitization of the grains — *T.H.J.*

Literature Cited: F. Evva, *Z. wiss. Phot.* 52: 1–24, 64–74, 136–57, 237–47 (1957–58). E. Brauer, *Phot. Korr.*, 94: 35–40 (1958). ———, *Sci. et inds. phot.*, 29: 161–7 (1958).

The Form of Developed Silver

As Dr. E. Klein demonstrates by means of some excellent electronmicrographs published in a paper[1] of the above title, the form of the developed silver can vary greatly depending on the composition of the developer. A change in the form of the silver can be brought about by a change in the concentration of the developing agent, a change in the pH of the solution or the nature of the developing agent, a change in the concentration of sulfite, or by adding thiocyanate to the solution.

Simple dilution of a Phenidone-ascorbic acid developer (no sulfite) caused the number of filaments to decrease and the length of the filaments to become greater, but the filament thickness remained unchanged. A decrease of 125 fold in the concentration of the developing agents in a Metol-hydroquinone solution of pH 10, with the sulfite content held constant, caused a shift in the form of the silver from fine filaments to much coarser threads. Increase in the sulfite content of a Metol developer, or addition of thiocyanate to such a developer, produced a shift in the same direction. A *p*-phenylenediamine developer of pH 9.5, which formed filamentary silver when the sulfite content was only 0.6 grams/liter, produced nonfilamentary particles of silver of very roughly spherical shape when the sulfite content was 60 grams/liter. A similar transition from filamentary to nonfilamentary silver was obtained with the Phenidone-ascorbic acid developer by adding 16 grams potassium thiocyanate per liter, or with a Metol-hydroquinone-sulfite developer by adding smaller amounts of thiocyanate. There appears to be a good correlation between the form of the developed silver and the extent to which solvent action occurs on the silver halide during development.

Klein uses the term *chemical* development to denote a process which yields thin filaments of silver that may be short or long, and that have a thickness of about 50 mμ. He uses the term *physical* development to denote the process which produces rounded silver aggregates which do not show growth in any preferred direction. He considers three possible modes of development: (1) The rate of chemical development is much higher than the rate at which the silver halide is dissolved and hence much higher than the rate of physical development. The silver formed is filamentary. (2) The rate of solution of the silver halide and hence the rate of physical development is higher than the rate of chemical development. Development centers separate from the grain and grow by physical development without preferred direction. (3) The rate of solution of silver halide is comparable to the rate of chemical development. Filaments are formed by chemical development and additional silver is deposited on them by physical development. The filaments thus become thicker than those formed by chemical development alone.

The general results obtained by Dr. Klein, and his conclusions as to how the various forms of image silver are produced, are in good agreement with results reported independently by James and Vanselow[2] on the color and morphology of developed silver, and by James[3] on the kinetics of development by *p*-phenylenediamine. The term *solution-physical development* is used in the latter papers to designate the process which Klein refers to as physical development.

In another paper, Klein[4] describes the use of a developer which produces substantially pure (solution-)physical development to determine the number of nuclei formed by the action of x-ray, high-intensity light, and normal-intensity light exposures on photographic grains. The developer consists of: Metol, 7.5 grams; sodium sulfite, 60 grams; and potassium thiocyanate, 10 grams per liter, with a pH of about 7. The size of the developed silver particles decreased and their number increased with increasing levels of exposure. The latent image formed by high-intensity light and x-ray was more dispersed than that formed by normal-intensity light. This latter result is in agreement with results obtained by Hoerlin and Hamm,[5] who used a gold-intensification procedure to make the latent image nuclei large enough to be resolved by the electron microscope.

References 1. E Klein, *Z. Elektrochem.*, 62: 505–19 (1958); *Mitteilungen Forschungslab. Agfa Leverkusen*, 2: 43–79 (1958). (An abridged version of this paper was presented at the Annual Conference of the SPSE in Rochester, N.Y., Oct. 9. 1958.) 2. T. H. James and W. Vanselow, *Phot. Sci & Eng.*, 1: 104–18 (1958). 3. T. H. James, *J. Phot. Sci.*, 6: 49–56 (1958). 4. E. Klein, *Z. Elektrochem.*, 62: 870–73 (1958). 5. H. Hoerlin and F. A. Hamm, *J. Applied Phys.*, 24: 1514–19 (1958).

Static Markings on Film

Static discharges can produce a variety of beautiful but unwanted markings on photographic film. The markings can take various shapes. The familiar tree-like branching is often obtained, but feathers,

streaks, and blotches also can be formed by static. The causes, and some means of prevention, of static markings on motion-picture film are discussed in a recent paper by W. I. Kisner. The pattern obtained depends on whether the film is positively or negatively charged, on the composition of the support, on the nature of the emulsion or backing application, and on the type of material which comes in contact with the film. In another paper on static marks, Ryobun Seimiya describes and illustrates the markings produced under various conditions by a voltage surge from a Wimshurst induction machine. The film was placed on, or at various distances above, a metal plate connected to the machine, and the discharge was induced by bringing a grounded metal plate in contact with the film. The tree-like markings appeared when the film was negatively charged; the feather- and spot-shaped marks were produced when the film was positively charged. Line- or spot-shaped marks appeared when the charged film was touched with a conductor which had a smaller charge, and the markings did not depend on the sign of the charge. Both papers are well illustrated with reproductions of an assortment of static marks produced in various ways. Seimiya's paper, in Japanese, has an English summary, and the captions of the figures, including drawings of the experimental arrangements, are in English. —*T.H.J.*

Literature cited: W. I. Kisner, *J. Soc. Mot. Pic. TV Engrs.*, *67:* 513–17 (1958). R. Seimiya, *Konishiroku Rev.*, *8:* 60–75 (1957).

Stability of the Latent Image and of Photolytic Silver

The remarkable stability of the latent photographic image towards certain types of chemical change in its surroundings is discussed by Dr. J. Eggert in a paper of the above title, and is illustrated by experimental results presented in another paper by Dr. Eggert and H. Fischer. It is well known that at least a portion of the latent image will survive complete removal of the silver halide by a suitable solvent, and can subsequently be physically developed. Eggert and Fischer have shown that the latent image formed in certain silver chloride emulsions retains in all details its characteristics as a catalyst for chemical development even after the silver chloride has been converted to silver bromide by bathing the exposed emulsion in a potassium bromide solution. The silver bromide emulsion obtained by conversion of the silver chloride to bromide *before* exposure showed characteristic differences from the chloride emulsion in latent image formation, and in susceptibility to the Herschel effect and to the Sabattier effect. However, latent image formed in the silver chloride remained typical of the silver chloride emulsion in all three respects even after the chloride has been converted to bromide. Once the latent image had been formed, apparently the silver halide served only as a source of silver for development.

An interesting result was obtained with a silver thiocyanate emulsion. No direct development could be obtained, because the developer reduced the silver thiocyanate independently of whether or not it had been exposed to light. However, latent image was formed in the silver thiocyanate by the action of light, and it could be satisfactorily developed after the silver thiocyanate had been converted to silver bromide.

Some experiments carried out with A. Büchler on the Weigert effect in print-out silver are briefly discussed by Eggert. The print-out silver formed in some silver chloride emulsions retained its polarizing properties to a considerabe degree (e.g. up to 70% in some instances) even after the silver chloride had been removed by a solvent or had been converted to silver bromide or iodide. Apparently the structure of at least part of the print-out silver remained unaltered by these processes. —*T. H. J.*

Literature cited: J. Eggert, *Z. Elektrochem.*, *62:* 48–9 (1958). ———, and H. Fischer, *ibid.*, 230–5, 393–400 (1958).

Hypersensitizing Infrared Film

S. M. Solov'ev, in *Zhur. Nauch. i Priklad. Fotografii i Kinematografii*, *3:* 223-4 (1958), recommends the following solution for hypersensitizing infrared film: 1.5 ml of 1% silver nitrate solution, 0.75 ml of 25% aqueous ammonia, and water to make 100 ml. The film or plates are bathed in this solution for 4 min, rinsed in a water-alcohol 1:1 mixture, and dried rapidly. In the following issue of the same journal, p. 285, Solov'ev and N. M. Parfenova report that stable hypersensitized films can be obtained by following the 4-min treatment in the above solution by a 1-min water rinse and a 4-min immersion in a bath containing 5 to 8 ml (depending on the degree of fogging of the film) of a 1% aqueous solution of the stabilizer, 5-methyl-7-hydroxy-1,3,4-triazaindolizine diluted to 100 ml with water. The film is then rinsed in the water-alcohol mixture and dried rapidly. —*T.H.J.*

PHOTOGRAPHIC SCIENCE AND ENGINEERING
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• Technicalia Photographica

FRANK SMITH

Camera Gives Panoramic View of a Typhoon's Eye

A new way of gaining better understanding of typhoons and other disastrous cyclonic storms is being developed through the use of a unique horizon-to-horizon aerial camera.

Making possible this type of study is a high-resolution camera designed and built by the Perkin-Elmer Corp., Norwalk, Conn. Unlike conventional cameras, the Perkin-Elmer Corporation's Panoramic Tracking Camera employs a rotating prism to "wipe" the image on film. It covers, on each exposure, 180° horizon-to-horizon perpendicular to the plane's flight path, and 42° with the flight path. The camera carries enough film for a complete mission, and can be set to take either adjacent or stereo-overlapping photographs automatically.

The camera, flown by the U.S. Air Force Air Weather Service last November over Typhoon "Kit," for the first time gave meteorologists a panoramic view of a typhoon's eye in its entirety. From an altitude of approximately 55,000 ft, it showed the 30-mile wide center of "Kit" and the surrounding area.

The dark areas in the accompanying photograph are the sea. The tops of the clouds in the upper center are at 48,000 ft. The mid-vertical of the picture, from top to bottom, covers 39 nautical miles. The middle third, from top to bottom, shows a nearly correct view downward, but from side to side it slopes off toward the horizons.

Cinegrafic CE-260 Datapulse Camera

The Cinegrafic CE-260 Datapulse is a new pulse camera of small size which features pulse rates up to 24 frames/sec and cine rates up to 48 frames/sec. The camera uses standard 35mm film, 1600 frames per load of 60 ft, is daylight loading, and produces pictures slightly larger than half-frame, measuring 0.410 × 0.968 in. It accepts the Eyemo standard lens mount, other mounts being optional. Interchangeable shutters with 1° to 180° openings are available. The film transport is of the intermittent sprocket-movement type with 0.01-sec maximum pulldown time.

The camera operates on 28v d-c, 1 amp maximum load. It is $6^1/_2 \times 5^3/_8 \times 4^{23}/_{32}$ in. deep and weighs $4^3/_4$ lb fully loaded. The camera is designed for ground or airborne use.

Additional information may be obtained from Traid Corp., 17136 Ventura Blvd., Encino, Calif.

New Polaroid Land Camera Model 110A (The Pathfinder)

A new version of the Polaroid "Pathfinder" Land Camera has been announced by Polaroid Corp., Cambridge 39, Mass.

Known as Model 110A, this latest Polaroid Land Camera offers as wide a range of lens openings and shutter speeds as the earlier version (Model 110) but, in addition, features a completely redesigned coupled range-finder and a new automatic parallax-correcting viewfinder. It produces a $3^1/_4 \times 4^1/_4$-in. print 1 min after the picture is snapped.

The Model 110A has a 127mm $f/4.7$ Rodenstock lens with click stops at half-stop intervals to $f/45$. Resolving power of the 4-element coated and color-corrected lens is 70 lines/mm. or better. The camera is equipped with a six-blade Prontar shutter with nine speeds from 1 sec to $^1/_{300}$th plus "bulb," and provides the "EV" (Exposure Value) numbering system.

In addition to a 10-sec-delay self-timer, it has full M-X synchronization at all speeds so that all types of flash bulbs and electronic flash units may be used.

New Polaroid Land 4 × 5 Film Holder

A new Polaroid Land 4 × 5 Film Holder which instantly adapts a 4 × 5-in. camera for 60-sec pictures, has been announced. This new holder is interchangeable with regular film holders with no change in film plane and no adjustment of rangefinder or ground glass. The holder remains in the camera for reshooting. A new specially designed 4 × 5-in. film packet contains negative, positive sheet, and developing pod — the elements necessary for making 60-sec pictures.

The film holder conforms to ASA specifications for cameras and instruments designed to use 4 × 5 film holders of the lock rib type. It will fit press and view cameras equipped with Graphic, Graflok, and similar backs. The holder, which weighs 24 oz, is constructed of die-cast aluminum and the built-in stainless steel processing rollers are ball-bearing mounted.

Polaroid's New 4 × 5 Sheet Films

New sheet films for use in the holder described above are similar to previous Polaroid products in principle. Instead of being in rolls, however, a single negative, its positive print sheet, and a pod of developer have been combined in a light-tight paper envelope. The unit is called a film packet.

Once the holder is on the camera, individual film packets are shoved into it, exposed, pulled out, and processed as fast as the photographer can go through the simple operating routine. Even when films are processed immediately, picture taking is not restricted to one a minute.

There are two film types: Polaroid Pola Pan Land Packet, Type 52, which has its negative material coated on a paper base and is essentially the same as the popular Pola Pan 200 roll film; and Polaroid Professional Pan Land Film, Type 53, which has an acetate film base negative. Both types have an exposure index of 200 for daylight, 160 for tungsten light. The actual picture size is $3^1/_2 \times 4^1/_2$ in.

Photography at Woods Hole

The October issue of *Oceanus* (Vol. 6, No. 1, 1958), the quarterly periodical published by the Woods Hole Oceanographic Institution, Woods Hole, Mass., is entirely devoted to photography at Woods Hole.

With emphasis on underwater aspects, the issue contains a collection of unique photographs, many of which have already appeared in the scientific literature, popular periodicals, encyclopedias, textbooks, etc., while others have never before been published.

The technical articles on photography published in this issue of the periodical include "The Camera as a Tool," by Claude Ronne; "30,000 Photos a Second Two Miles Down," Anonymous; "Electron Micrographs of Diatoms," by Joyce C. Lewin and Delbert E. Philpott; "The Luminescence Camera," by George L. Clarke; "Photography of the Sea Floors," by J. A. Posgay; and "Photography Underwater," by D. M. Owen.

Two New Cameras from Germany

Zeiss Ikon AG., Stuttgart, Germany, have announced two new 35mm still cameras, the Contarex and the Ikonette.

The Contarex is a 35mm single-lens reflex camera with focal plane shutter, interchangeable Carl Zeiss lenses and coupled exposure meter.

The manufacturer states that the design of the new Contarex is based on the working principles of the Contaflex and the Contax. In addition, many new features have been incorporated. The normal lens is an *f*/2 Planar 35mm. Other interchangeable lenses available are the *f*/4.5 Biogon 21mm with an extreme angle of 90 degrees, the *f*/4 Distagon 35mm, the *f*/2 Sonnar 85mm, the *f*/4 Sonnar 135mm, and the *f*/4 Sonnar 250mm. All lenses have a helical mount with straightline motion. Shutter speeds up to 1/1000 sec, rapid-wind lever, built-in photoelectric exposure meter, and a viewfinder whose image is upright, unreversed and brilliant up to the corners are features of the Contarex.

The Ikonette is a 35mm camera of interesting modern design. A feature of the camera is the combined rapid-wind and release lever which facilitates its rapid use. The Ikonette is equipped with a Prontor shutter with speeds up to 1/200 sec, a delayed action timer, and a Novar anastigmat *f*/3.5 45mm lens. The body of the camera is two-tone gray plastic.

Opta-Vue Micro-Reader, Model F

Optics Mfg. Corp., Industrial Div., Philadelphia 34, Pa., has developed a handy little streamlined tool for data reduction called the Opta-Vue Micro-Reader Model F. The company states that it is the only

handheld Micro-Reader specifically designed for film reading. Used for quick reference or sustained work, the Micro-Reader produces sharp clear images. It accepts aperture cards and jacketed strips up to 70mm wide. Interchangeable objectives for various reduction rates are available.

General Electric AG New (All Glass) Flash Bulb

A tiny flash bulb, said to be the smallest ever produced in the U.S., has been developed by the General Electric Co., Lamp Dept., Nela Park, Cleveland, Ohio.

The flash bulb, made entirely of glass including the base, is only $1\frac{1}{8}$ in. long and $\frac{3}{8}$ in. in diameter.

Using a zirconium filling, the bulb is claimed to be as bright as the M2 bulb which is four times larger.

Reports indicate that GE is considering the possibility of manufacturing the bulbs in a plastic clip holding six or more. The clip could be stored in a special flash gun and the bulbs fired in repeater fashion. After firing all the bulbs, the flash gun would be reloaded simply by inserting another clip of lamps.

Reproduction of Colour

R. W. G. Hunt, *Research* (London), *11:* 432–438 (1958).

A brief review of the history and current methods of reproducing color with particular reference to photography, television, and printing. The article is based on the author's book, *The Reproduction of Colour* [reviewed in *P S S E*, 2: 235 (Dec. 1958)], and it will be followed by an article in which Dr. Rushton of Cambridge University discusses the chemical basis of human color vision. Ill., 4 ref.

FLIP (Film Library Instantaneous Presentation)

Benson-Lehner Corp., 11930 W. Olympic Blvd., Los Angeles 64, Calif., has developed an automatic microfilm searching machine for information retrieval involving large masses of documents. Called FLIP (Film Library Instantaneous Presentation), the machine was designed for a specific application and not to solve the general information retrieval problem. In FLIP, the prime design criterion was to develop a machine to search for a particular frame of 16mm film at the comparatively high speed of 300 to 600 frames/sec and then to present this frame, containing pictorial data and binary coded information, to the operator for viewing.

Upon command to search, the machine chooses the correct direction for search and, upon recognizing the frame, stops, overshoots about five frames, and returns to project the image on the screen for visual presentation. The film transport is designed to accommodate 1200 ft of 16mm double-perforated film, containing up to 72,000 frames. The film is scanned at a minimum speed of 60 in./sec. During the scanning interval, photosensitive elements simultaneously read coded binary digits represented by the presence or absence of code bars adjacent to each film frame presentation.

The image is enlarged approximately 50 diameters on the rear of a back-lighted screen without appreciable loss of resolution or contrast. The resolution of the optical system is better than 25 lines/mm.

Mast Model 1001 High Speed Spot Scanner

The Mast Development Co., Inc., 2212 E. 12th St., Davenport, Iowa, has developed an instrument, Model 1001 High Speed Spot Scanner, for accurately checking

the shutter operation of the 0–15, 0–20, 0–30, 0–32 and similar cameras used in radar recording systems. Shutter-open and shutter-closed time periods can be read within 0.001 sec, directly from film exposures made of the High Speed Spot Scanner's animated display.

The display consists of a circular scale engraved on a flat transparent ring. The circumference is graduated in 200 increments of 0.001 sec each. A 0.020-in. diameter light spot rotates 5 times/sec behind the transparent scale. The scale and the light path formed by the rotating light spot are simultaneously exposed on the film of the camera being tested, at a speed of 5 frames/sec. The length of the path traced on any given frame of the film by the rotating light spot can be read along the scale as the shutter open time.

The shutter closed interval between any two consecutive frames is determined by the difference in scale reading from the end of the trace made by the rotating spot on one frame to the beginning of the trace on the succeeding frame.

The Model 1001 High Speed Spot Scanner is approximately 25 in. long, including the periscope which is used in mounting the cameras. A special adapter kit is available for using the High Speed Spot Scanner with the 0–20, 0–23 and 0–32 cameras.

RCA "Intensifier" Orthicon

A new developmental, advanced type of camera tube, based on television principles, has been announced by RCA.

The new tube is an extremely sensitive electronic eye which may permit visual reconnaissance in almost total darkness. Heart of the new tube is one or two "intensifier" stages between the light-sensitive pickup surface at the front of the tube and the signal output assembly at the rear. The new tube is said to be probably 100 times more sensitive than the fastest known photographic film for the same exposure time at low levels of light. Development of the tube was sponsored by the Aeronautical Research Laboratory, Wright Air Development Center.

Correction

The temperature limit of performance of Wollensak Optical Company's new Periscopic Lens was incorrectly given as 100° F on p. 237 of the December 1958 issue (Vol. 2, No. 4). The temperature should be listed as approximately 1000° F.

• Notes from the Editor

Six Issues for 1959

Volume 3 of *P S & E* will contain six issues. It is hoped to publish these issues at regular intervals of two months each.

Medical and Biological Illustration

This unique journal has been published by the British Medical Association under the able editorship of Dr. Peter Hansell since the journal was founded in 1950. With the completion of Volume 8, Dr. Hansell relinquishes his duties as Editor, but will remain on the Editorial Board. The new Editor is C. E. Engel, Chief Photographer to the Medical School, Guy's Hospital, London. Peter N. Cardew has been appointed as an assistant editor.

Bausch & Lomb Optical Company

The name of Bausch & Lomb Optical Company was inadvertently omitted from the list of Sustaining Members published in Volume 2, Number 4. We regret this omission and extend our apologies.

T. H. James

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